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## MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1681

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# UTILIZATION OF NONPETROLEUM FUELS IN AUTOMOTIVE ENGINES

By Jesse T. Duck and Clarence S. Bruce

ABSTRACT

A number of substitute fuels and blends were tested to determine their relative efficiency in the operation of common types of engines. The tests showed that the maximum power developed with alcohol and with some of the other fuels was slightly greater than with gasoline. The specific fuel consumption with the various fuels was approximately in inverse proportion to the heat of combustion of the fuel used. Analysis showed that the mixture distribution was less uniform with the substitute fuels than with gasoline. Tests made with low-proof alcohols showed than an engine can be operated on blends as low as 70 proof, but it is ordinarily impractical to use a blend much below 190 proof because of the excessive volume required.

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## I. INTRODUCTION

The tests reported herein are part of an extensive study [1][1] of substitute motor fuels conducted by the National Bureau of Standards for the Foreign Economic Administration. The fuels used in this

[1] Figures in brackets indicate the literature references at the end of this paper.

phase of the study were ethyl alcohol and related compounds, either in their relatively pure state or in blends with water or with each other. Particular attention was given to 190-proof and 200-proof alcohol. The principal objectives of this part of the investigation were to show (1) the comparative performance of various engines and fuels with respect to power and fuel economy, (2) the relation of combustion temperatures to air-fuel mixture ratios, (3) the relative efficiency of mixture distribution with various fuels, and (4) the relation of air-fuel ratio to exhaust-gas composition.

## II. FUELS USED IN THE TESTS

The fuels used in the tests were (1) 190-proof alcohol, (2) 200-proof alcohol, (3) acetone, (4) *N*-butanol (normal butyl alcohol), (5) "No. 1 Blend"—a blend containing 50 percent of acetone and 50 percent by volume of butanol, (6) "No. 2 Blend"—a blend of 67 percent of butanol, 27 percent of acetone, and 6 percent of ethanol, (7) "No. 3 Blend"—a blend of 71.5 percent of butanol and 28.5 percent of acetone, (8) a blend of 20 percent of diethyl ether and 80 percent of 190-proof alcohol, (9) various low-proof alcohol blends, and (10) gasoline.

## III. TEST EQUIPMENT

### 1. ENGINES AND ACCESSORIES

Two 1942 Plymouth engines, a 1942 Chevrolet, and a 1940 Ford V–8 engine were used. The engines were coupled to electric dynamometers, equipped with dynamometer scales. Special test equipment included instruments for measuring oil pressure and cooling water temperatures, thermometers for measuring the temperatures of the fuel and air, a volumetric fuel-measuring device, and thermocouples for measuring various engine temperatures.

### 2. THERMOCOUPLE SPARK PLUGS

The spark plugs used in the tests were of the type devised by Rabezzana and Kalmar [2]—a special-type plug with tubular center electrodes into which iron-constantan thermocouples are inserted and welded to the electrode near its tip. The purpose of using these spark plugs was to study the mixture distribution. Rabezzana and Kalmar found that the temperature measured at the tip of the electrode is strictly proportional to the mean combustion temperature and very sensitive to changes in mixture ratio. This being true, this temperature can be used for determining mixture conditions by correlation of temperature changes with changes made in mixture ratios or other operating conditions.

The temperatures indicated by spark-plug thermocouples in different cylinders should not be regarded as directly comparable, because it is unlikely that two thermocouples can be located in the same positions relative to the tip and walls of the electrodes. The temperature drop along the electrode is very sharp so that a very small shift in the position of the thermocouple in the electrode might make a difference of 50 to 100 degrees in its indicated temperature.

### 3. CARBURETION

To facilitate changing the mixture ratio, standard carburetors were modified to permit a greatly increased rate of flow, with the leaner mixtures being supplied by lowering the pressure in a sealed carburetor float bowl by suction from the venturi. A needle valve in the suction line was used to regulate the pressure drop in the bowl. Another needle valve in the top of the bowl was used as an air bleed for further control. The engine could then be operated over a wide range of mixture ratios.

### 4. EXHAUST-GAS ANALYZER

The Hays Orsatomat, used in analyses of the exhaust gas, removes the $CO_2$ from the sample by absorption. The resulting reduction in volume actuates a needle that indicates the percentage of $CO_2$. The instrument was frequently calibrated against known mixtures of $CO_2$ and air. The corrected readings are believed to be accurate within 0.5 percent.

### 5. AIR-FLOW INDICATOR

A calibrated flow indicator was used in the air measurements. The air is forced through it by a constant-speed fan whose output is controlled by a valve. The output of the instrument may be varied from about 5 $ft^3$/min to somewhat above 75 $ft^3$/min. The pressure at the carburetor air intake was kept balanced with the atmosphere by controlling the air flow. To guard against errors due to engine pulsations, a collapsible rubber sleeve was placed in a section of the air line.

## IV. OUTLINE OF TEST PROCEDURE

In the tests at full throttle the engine speed was kept constant at 1,500 rpm by making the necessary changes in the electric load of the dynamometer. The operating range of mixture ratios was estalished for each of the fuels by making a number of test runs in which the mixture ratio was varied in steps from lean to rich by use of the back-suction control of the carburetor. The power and specific fuel consumption were then plotted against the measured fuel consumption, the latter being an index of the mixture ratio in operation at any constant throttle setting. This is shown in figure 1.

In the road-load tests (part throttle) the same procedure was followed, except that the engine speed and dynamometer load were kept constant at the value calculated as equivalent to road operation at a given speed, and the throttle was varied to keep the desired speed and load as the mixture ratio was changed.

For each test run a set of data was recorded, including temperatures observed for each of the spark-plug thermocouples, exhaust, intake riser, oil, and water; also intake-manifold depression, float-bowl depression (back suction from the venturi), the time required to use a measured amount of fuel, and the speed and torque developed by the engine.

The spark advance was set for maximum engine power with the engine operating at 1,500 rpm on gasoline. With the first Plymouth

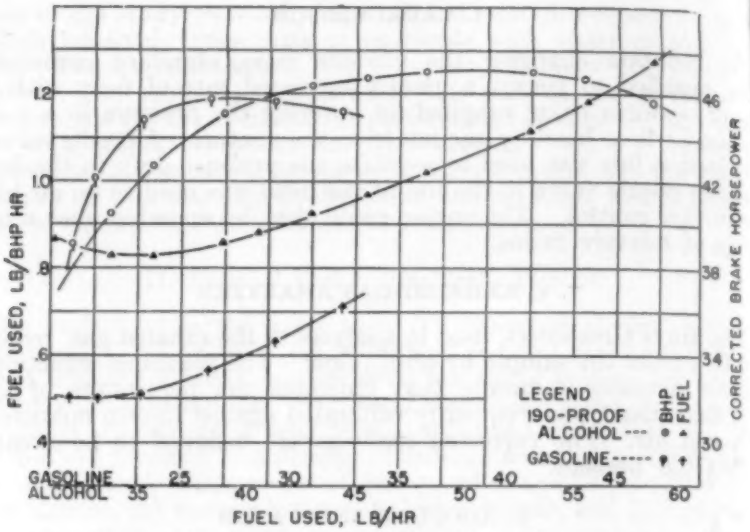


FIGURE 1.—*Power and specific fuel consumption for gasoline and 190-proof alcohol, 1942 Plymouth, test engine 4.*

The engine was operated at 1,500 rpm, full throttle, with the spark setting for maximum power.

test engine these settings were made by shifting the spark advance until the highest engine power was observed. Regular-grade gasoline of about 72 octane number was used. It was later discovered that this engine lost power because of excessive detonation when regular gasoline was used, and that the optimum spark advance was several degrees less than for fuels that did not cause detonation.

The optimum spark advance for the Chevrolet engine was also determined by observation. With the Ford V-8 engine and the second Plymouth engine (herein designated as test engine 4), the optimum spark advance was taken as the peak of a smooth curve joining the points when the observed power was plotted against the spark advance (see fig. 2). The optimum spark advance determined by this method for the various fuels ranged from 16.5 to 18.5 degrees with the Ford V-8 engine and from 16.4 to 19.0 degrees with the Plymouth engine. This variation was probably within the limits that might be accounted for by experimental error and by differences in atmospheric conditions. Therefore, the same spark advance was used for all the fuels except the low-proof alcohols, which required a definitely greater advance than the other fuels.

The optimum spark advance for low-proof alcohols of various proofs increased progressively from about 17 degrees with 200-proof alcohol to about 50 degrees with 70-proof alcohol, as shown in figure 3. The spark setting used in the part-throttle runs was that for maximum power with full throttle, as in road operation there is ordinarily no practical way to find the optimum spark advance at part throttle.

The air flow was measured in the road-load tests of the 1942 Plymouth engine and in some of the tests of the same engine at full throttle. The air-flow indicator was not available for use in the other tests.

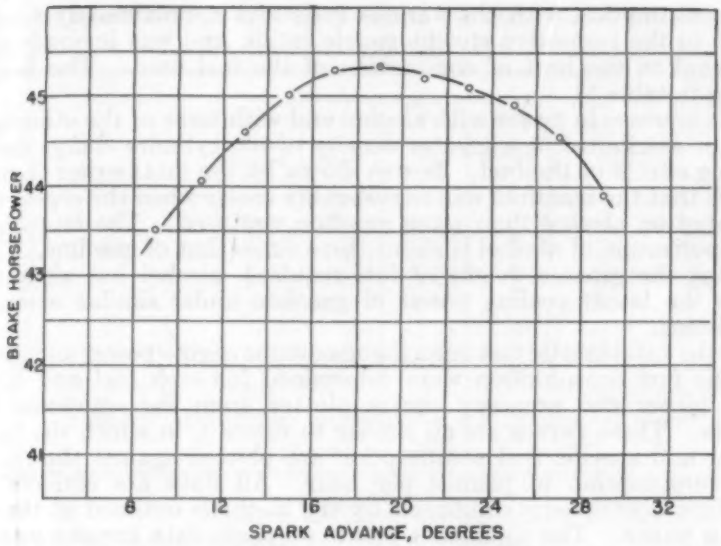


FIGURE 2.—*Spark advance and maximum engine power, 1942 Plymouth, test engine 4.*
The engine was operated at 1,500 rpm, full throttle on 190-proof alcohol.

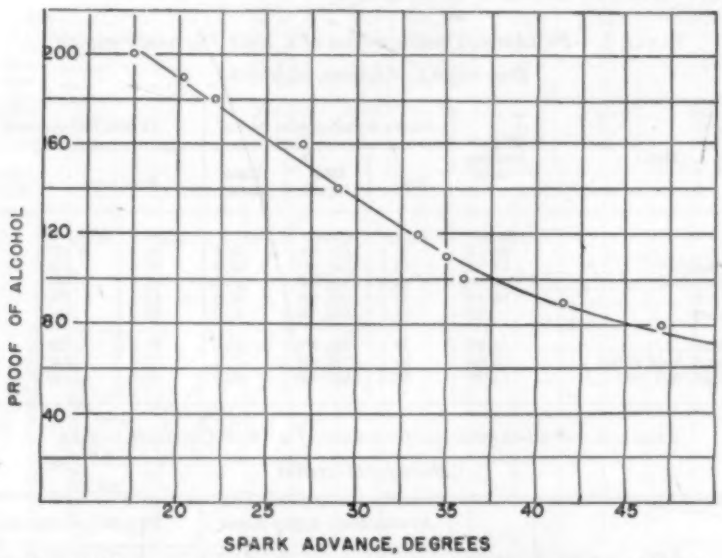


FIGURE 3.—*Optimum spark advance for alcohols of various proofs; 1942 Plymouth.*
The engine was operated at 1,500 rpm with full throttle.

## V. TEST RESULTS

### 1. FULL-THROTTLE POWER AND FUEL CONSUMPTION

In general the alcohol fuels and blends produced slightly greater engine power (up to about 4 percent), but required considerably more fuel than was used when the engine was operated on gasoline. The

fuel consumption with the various fuels was approximately proportional to the respective stoichiometric ratios, and was inversely proportional to the heat of combustion of the fuel used. This is best shown in table 11.

The increase in power with alcohol and with some of the other fuels may be attributed to a greater density of the cylinder charge due to cooling effects of the fuel. It was shown by the intake-riser thermocouple that the manifold was considerably cooler when the engine was operated on alcohol than when gasoline was used. The latent heat of vaporization of alcohol is about three times that of gasoline. Considering the greater weight of fuel required, alcohol has about five times the latent cooling power of gasoline under similar operating conditions.

In the full-throttle test runs the maximum engine power and lowest specific fuel consumption were determined for each fuel and engine from power and economy curves plotted from the computed test results. These curves are all similar to figure 1, in which the horsepower and specific fuel consumption are plotted against the rate of fuel consumption in pounds per hour. All data are corrected to standard atmospheric conditions by the methods outlined at the end of this paper. The significant points on these data are the maxima of the power and the minima of the economy curves. The values for maximum power and lowest specific fuel consumption from these plots are listed in tables 1, 2, 3, and 4.

TABLE 1.—*Full-throttle performance of a 1942 Plymouth engine*

[Test engine 1. 1,500 rpm, full throttle]

| Fuel | Higher heating value | At maximum engine power | | | At best fuel economy | | |
|---|---|---|---|---|---|---|---|
| | | Fuel | Heat input | Horsepower | Fuel used | | Thermal efficiency |
| | *Btu/lb* | *lb/hr* | *Btu/hr* | | *lb/hr* | *lb/bhp hr* | % |
| Gasoline | 20,120 | 28.5 | 572,850 | 47.8 | 23.4 | 0.525 | 24.0 |
| 200-proof alcohol | 12,720 | 42.8 | 543,144 | 50.0 | 32.8 | .725 | 27.6 |
| 190-proof alcohol | 11,760 | 43.4 | 510,380 | 49.0 | 33.3 | .735 | 29.4 |
| No. 1 Blend | 14,380 | 40.5 | 582,390 | 47.3 | 32.0 | .735 | 23.9 |
| No. 2 Blend | 14,650 | 38.0 | 556,700 | 47.2 | 30.7 | .695 | 25.0 |
| No. 3 Blend | 14,860 | 39.5 | 586,970 | 47.0 | 31.3 | .720 | 23.8 |
| No. 3 Blend, heat added | 14,860 | 39.7 | 589,940 | 47.0 | 32.0 | .740 | 23.1 |
| No. 3 Blend, full heat | 14,860 | 38.2 | 567,650 | 46.0 | 29.5 | .710 | 24.1 |

TABLE 2.—*Full-throttle performance of a 1942 Chevrolet engine*

[1,500 rpm, full throttle]

| Fuel | Higher heating value | At maximum engine power | | | At best fuel economy | | |
|---|---|---|---|---|---|---|---|
| | | Fuel | Heat input | Horsepower | Fuel used | | Thermal efficiency |
| | *Btu/lb* | *lb/hr* | *Btu/hr* | | *lb/hr* | *lb/bhp hr* | % |
| Gasoline | 20,120 | 27.4 | 551,300 | 46.5 | 22.3 | 0.515 | 24.6 |
| 190-proof alcohol | 11,700 | 46.0 | 541,000 | 46.8 | 36.5 | .853 | 23.4 |
| 200-proof alcohol | 12,720 | 44.0 | 559,700 | 47.8 | 35.5 | .807 | 24.8 |
| No. 1 Blend | 14,380 | 39.4 | 569,450 | 47.5 | 31.5 | .710 | 24.9 |
| No. 2 Blend | 14,650 | 38.6 | 565,490 | 47.4 | 31.6 | .700 | 24.8 |
| No. 3 Blend | 14,860 | 38.5 | 572,000 | 47.8 | 31.3 | .700 | 24.5 |
| Acetone | 13,180 | 42.0 | 553,560 | 46.8 | 34.7 | .800 | 24.1 |
| Butanol | 15,460 | 37.2 | 572,110 | 46.2 | 28.6 | .675 | 24.4 |

TABLE 3.—*Full-throttle performance of a 1940 Ford V–8 engine*

[1,500 rpm]

| Fuel | At maximum engine power | | | | At best fuel economy | | |
|---|---|---|---|---|---|---|---|
| | Higher heating value | Fuel | Heat input | Horsepower | Fuel used | | Thermal efficiency |
| | *Btu/lb* | *lb/hr* | *Btu/hr* | | *lb/hr* | *lb/bhp hr* | % |
| Gasoline | 20,120 | 29.0 | 551,014 | 43.7 | 21.7 | 0.538 | 23.5 |
| No. 1 Blend | 14,380 | 40.5 | 553,630 | 44.0 | 30.4 | .787 | 23.4 |
| No. 2 Blend | 14,650 | 39.0 | 556,700 | 43.9 | 30.2 | .738 | 23.5 |
| No. 3 Blend | 14,860 | 39.0 | 557,250 | 44.1 | 29.5 | .723 | 23.7 |
| Acetone | 13,180 | 43.5 | 548,970 | 44.3 | 33.5 | .835 | 23.1 |
| Butanol | 15,460 | 36.0 | 541,100 | 43.3 | 28.6 | .725 | 22.7 |
| 190-proof alcohol | 11,760 | 49.0 | 536,256 | 44.0 | 37.0 | .915 | 23.7 |
| 200-proof alcohol | 12,720 | 46.0 | 566,040 | 44.2 | 33.8 | .850 | 23.5 |

TABLE 4.—*Full-throttle performance of a 1942 Plymouth engine*

[Test engine 4. 1,500 rpm]

| Fuel | At maximum engine power | | | | At best fuel economy | | |
|---|---|---|---|---|---|---|---|
| | Higher heating value | Fuel | Heat input | Brake horsepower | Fuel used | | Thermal efficiency |
| | *Btu/lb* | *lb/hr* | *Btu/hr* | | *lb/hr* | *lb/bhp hr* | % |
| No. 1 Blend | 14,380 | 38.4 | 552,000 | 46.9 | 29.5 | 0.692 | 25.58 |
| No. 2 Blend | 14,650 | 38.0 | 556,700 | 46.9 | 29.0 | .680 | 25.55 |
| No. 3 Blend | 14,860 | 36.7 | 545,362 | 47.3 | 28.5 | .660 | 25.95 |
| Acetone | 13,180 | 43.4 | 572,000 | 47.4 | 33.6 | .770 | 25.08 |
| Butanol | 15,460 | 36.0 | 556,560 | 47.1 | 28.0 | .645 | 25.52 |
| Gasoline | 20,120 | 26.9 | 541,228 | 45.8 | 21.0 | .500 | 26.30 |
| 190-proof alcohol | 11,760 | 50.8 | 597,400 | 47.2 | 35.0 | .830 | 26.07 |
| 200-proof alcohol | 12,720 | 46.6 | 592,752 | 47.6 | 33.0 | .770 | 26.0 |

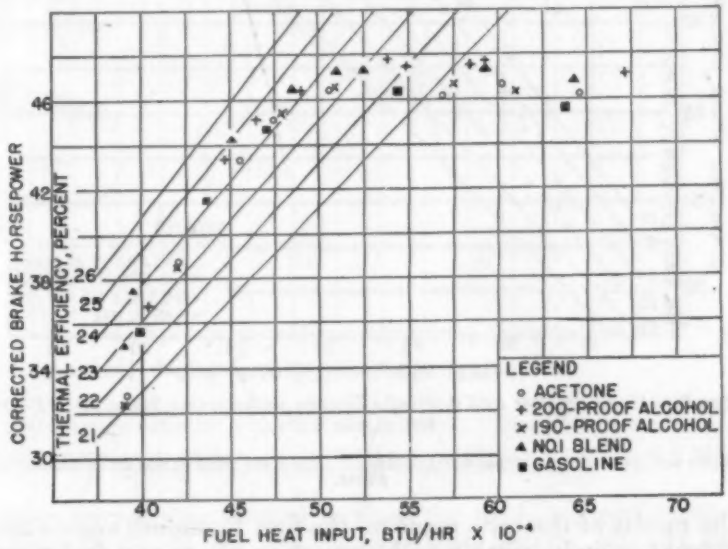


FIGURE 4.—*Engine power and thermal efficiency with various fuels, 1942 Chevrolet.*

The engine was operated at 1,500 rpm with full throttle. The spark advance was set for maximum engine power.

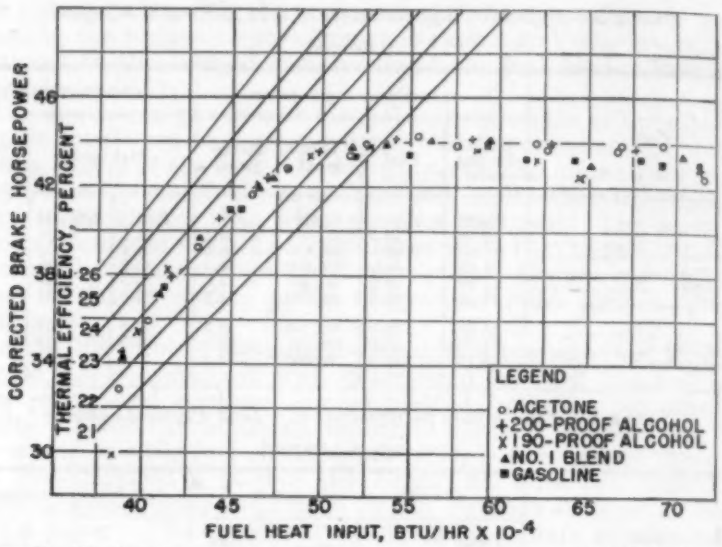


FIGURE 5.—*Engine power and thermal efficiency with various fuels, 1940 Ford V–8.*

The engine was operated at 1,500 rpm with full throttle. The spark advance was set for maximum engine power.

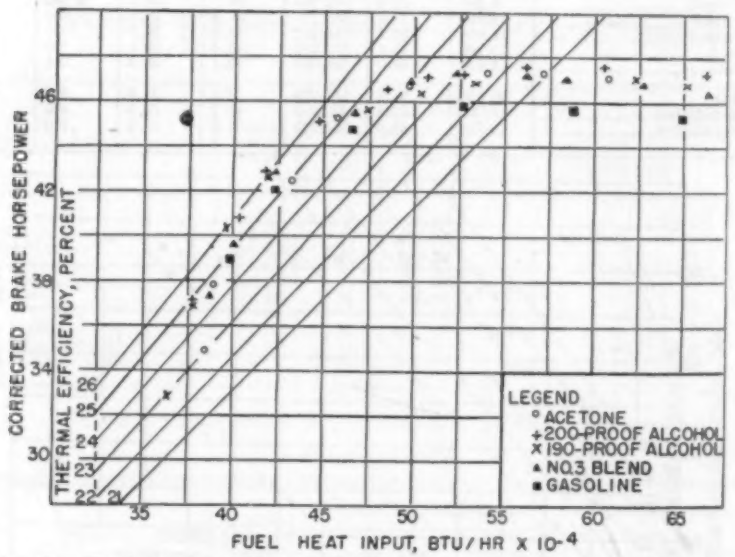


FIGURE 6.—*Engine power and thermal efficiency with various fuels, 1942 Plymouth, test engine 4.*

The engine was operated at 1,500 rpm with full throttle. The spark advance was set for maximum engine power.

The results of the tests made on the first Plymouth engine are not considered entirely reliable with respect to power and fuel measurements. The spark was retarded several degrees from that for best performance because of knock on regular gasoline, and the results of

some of the tests are inconsistent. The power developed with 190- and 200-proof alcohol appeared to be too high, but check runs were not possible because of an engine breakdown, which made major repairs necessary. These data are included in the report because some of the tests, not repeated on the other engines, contain useful information.

Figures 4, 5, and 6 show the power of three of the engines tested as related to fuel heat input and thermal efficiency.

## 2. ROAD-LOAD POWER AND ECONOMY TESTS

The results of the road-load power and economy tests of the Plymouth engine are shown in table 5. The data were taken from curves plotted from the test results. These curves show the relation of the intake-manifold depression and specific fuel consumption to the air-fuel ratio when the engine is operated with a constant speed and load equivalent to level-road operation at a given car speed. The highest manifold depression indicates the point on the mixture-ratio curve at which the desired load and speed can be maintained with a minimum throttle opening. This condition corresponds to that of maximum power for a fixed throttle opening and constant speed. Figures 7, 8, 9, and 10 show the manifold depression, specific fuel consumption, and percentage of $CO_2$ with the engine operating at 40 mph with varying air-fuel ratios.

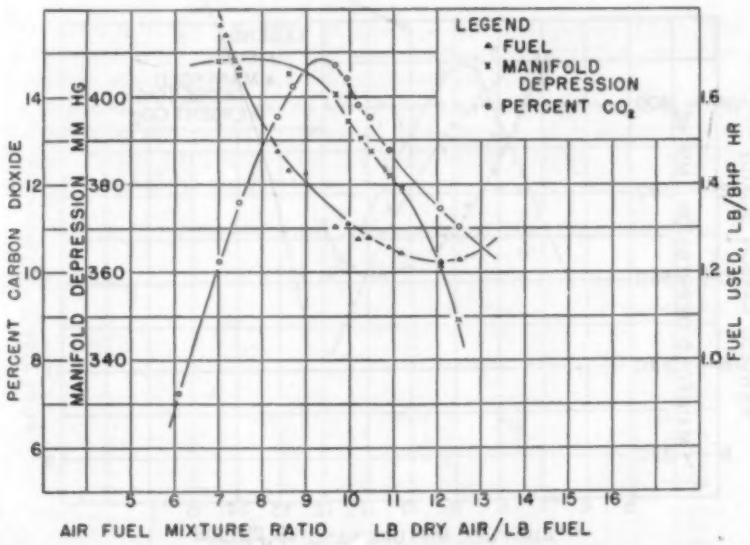


FIGURE 7.—*Manifold depression, percentage of* $CO_2$, *specific fuel consumption, and mixture ratio for 200-proof alcohol, 1942 Plymouth, test engine 4.*

The engine was operated at speed and load calculated as equivalent to road operation at 40 mph. The spark was set for maximum power at 1,500 rmp, full throttle.

Sixteen curves were plotted to show the road-load performance of four fuels at 20, 30, 40, and 50 mph with varying mixture ratios. The significant points on these curves were (1) the peaks of the manifold-depression curves which show the mixture ratio at which

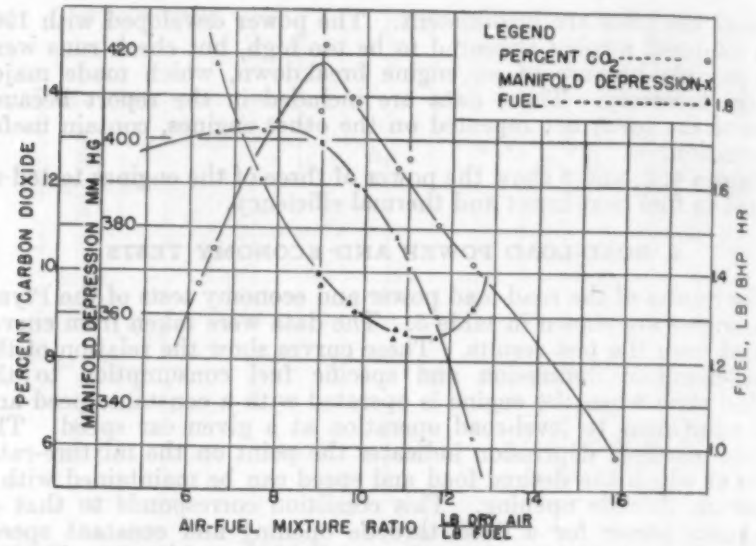


FIGURE 8.—*Manifold depression, percentage of $CO_2$, specific fuel consumption, and air-fuel ratio with 20-percent-ether blend; 1942 Plymouth, test engine 4.*

The engine was operated at speed and load calculated as equivalent to road operation at 40 mph. The spark was set for maximum power at 1,500 rmp, full throttle.

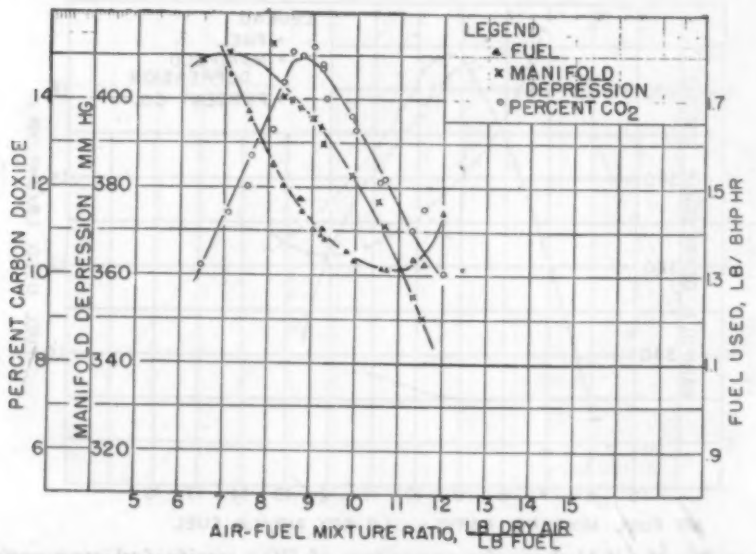


FIGURE 9.—*Manifold depression, percentage of $CO_2$, specific fuel consumption, and air-fuel ratio with 190-proof alcohol; 1942 Plymouth, test engine 4.*

The engine was operated at speed and load calculated as equivalent to road operation at 40 mph. The spark was set for maximum power at 1,500 rpm, full throttle.

the engine will hold the required speed and load with minimum throttle opening, and (2) the lowest point on the fuel-economy curve which shows the mixture ratio at which the fuel gives its maximum miles per gallon.

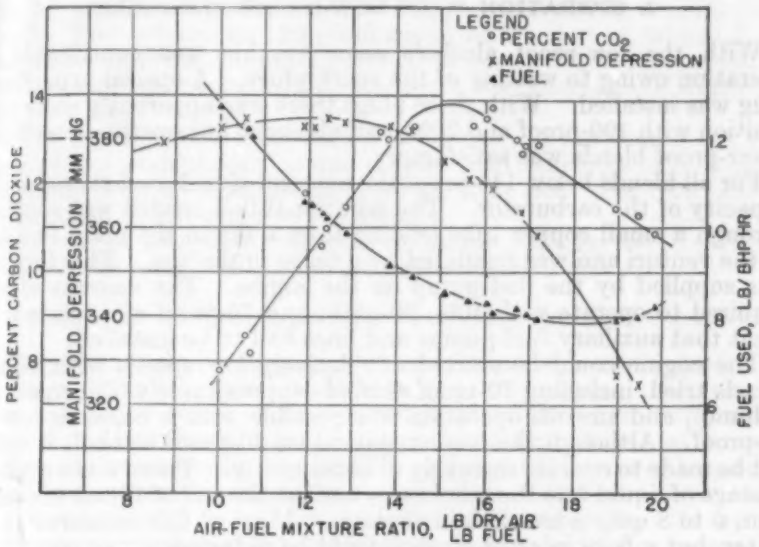


FIGURE 10.—*Manifold depression, percentage of* $CO_2$*, specific fuel consumption, and air-fuel ratio with gasoline; 1942 Plymouth, test engine 4.*

The engine was operated at speed and load calculated as equivalent to road operation at 40 mph. The spark was set for maximum power at 1,500 rpm, full throttle.

The fuel mileages shown in table 5 are computed from the fuel consumption for best economy and minimum throttle, as shown by the curves, assuming a fuel temperature of 77° F.

As in the full-throttle runs, the weight of fuel consumed is in inverse proportion to the heating value of fuel used and is approximately in the same direct proportion as the combining weights of the fuels with oxygen in complete combustion.

TABLE 5.—*Road-load power and economy of 1942 Plymouth engine*

[Test engine 4]

| Fuel | Car speed | At best fuel economy | | | At minimum throttle | | |
|---|---|---|---|---|---|---|---|
| | | Mixture ratio | Fuel used | | Mixture ratio | Fuel used | |
| | *mph* | | *lb/bhp hr* | *mpg* | | *lb/bhp hr* | *mpg* |
| Gasoline | 20 | • 16.5 | 1.135 | 26.3 | 12.6 | 1.390 | 21.5 |
| Do | 30 | 16.4 | 0.940 | 23.8 | 12.2 | 1.195 | 18.8 |
| Do | 40 | 18.0 | .795 | 21.4 | 12.0 | 1.063 | 15.8 |
| Do | 50 | 17.8 | .700 | 18.2 | 12.0 | 0.960 | 13.3 |
| 190-proof alcohol | 20 | 10.25 | 1.880 | 18.0 | 7.7 | 2.250 | 15.0 |
| Do | 30 | 10.6 | 1.540 | 16.6 | 8.0 | 1.785 | 14.2 |
| Do | 40 | 10.65 | 1.320 | 14.5 | 7.4 | 1.685 | 11.4 |
| Do | 50 | 10.5 | 1.185 | 12.2 | 7.4 | 1.490 | 9.8 |
| 200-proof alcohol | 20 | 10.5 | 1.730 | 19.2 | 8.2 | 2.040 | 16.4 |
| Do | 30 | 11.2 | 1.460 | 17.1 | 8.0 | 1.750 | 14.3 |
| Do | 40 | • 12.0 | 1.220 | 15.3 | 7.9 | 1.550 | 12.1 |
| Do | 50 | 11.1 | 1.120 | 12.7 | 7.8 | 1.400 | 10.1 |
| 20% ether, 80% 190-proof alcohol | 20 | 10.4 | 1.800 | 18.6 | 8.1 | 2.050 | 16.4 |
| Do | 30 | 11.35 | 1.465 | 17.2 | 8.3 | 1.730 | 14.5 |
| Do | 40 | 11.4 | 1.255 | 15.1 | • 7.7 | 1.600 | 11.8 |
| Do | 50 | 11.0 | 1.150 | 12.5 | 8.1 | 1.360 | 10.5 |

• Curve not definite at this point.

### 3. OPERATION WITH LOW-PROOF ALCOHOLS

With the low-proof alcohols some trouble was experienced in operation owing to wetting of the spark plugs. A special type "hot" plug was installed. With these plugs there was apparently some preignition with 190-proof and 200-proof alcohols, but operation with the lower-proof blends was satisfactory.

For all blends below 140-proof the amount of fuel used exceeded the capacity of the carburetor. The additional fuel needed was supplied through a small copper tube leading from a tee in the main fuel line to the venturi and was regulated by a valve in the line. This fuel line was supplied by the fuel pump on the engine. The amount of fuel required to operate with 100-, 90-, 80-, and 70-proof alcohols was so great that auxiliary fuel pumps and lines had to be installed.

The engine could be started at relatively low speeds with all the blends tried, including 70-proof alcohol (approximately 35 percent by volume), and smooth operation was possible with a blend as low as 80-proof. Although the engine started on 70-proof alcohol, it could not be made to operate smoothly or consistently. There was a gradual passage of liquid into the crankcase, until at the end of 1 hour of operation, 6 to 8 quarts had leaked through. Most of this appeared to be water, but a faint odor of alcohol could be detected.

The thermocouple spark plugs could not be used with the low-proof alcohols, so the mixture distribution could not be analyzed by combustion-temperature relationships, as in the case of the other fuels. It appeared, however, that distribution was very poor with the lower-proof alcohols, possibly because of the method of supplying the additional fuel required. In some cases there was a definite increase in power and smoother engine operation when the auxiliary fuel-supply tube was moved to a slightly different position in the venturi. Table 6 is a summary of the test results with respect to power, fuel consumption, and spark advance.

TABLE 6.—*Summary of tests of low-proof alcohols of various proofs*

[Test engine 4. 1942 Plymouth. 1,500 rpm, full throttle]

| Approximate proof of alcohol | Maximum power conditions | | | Gallons per hour of blend | Thermal efficiency | Optimum spark advance |
|---|---|---|---|---|---|---|
| | Brake horsepower | Ethanol | Ethanol | | | |
| | | *lb/hr* | *lb/bhp hr* | | | *Degrees* |
| 200 | 47.57 | 45.0 | 0.944 | 6.85 | 21.2 | 17.5 |
| 190 | 46.18 | 47.5 | 1.029 | 7.53 | 19.4 | 20.4 |
| 180 | 45.67 | 47.5 | 1.042 | 7.94 | 19.2 | 21.3 |
| 160 | 45.07 | 50.8 | 1.127 | 9.52 | 17.8 | 27 |
| 140 | 45.48 | 52.83 | 1.162 | 11.33 | 17.2 | 29 |
| 120 | 43.60 | 52.63 | 1.207 | 12.90 | 16.6 | 33 |
| 110 | 42.0 | 53.66 | 1.278 | 14.53 | 15.6 | 35 |
| 100 | 42.94 | 63.98 | 1.490 | 19.0 | 13.4 | 36 |
| 90 | 42.35 | 54.06 | 1.277 | 17.9 | 15.6 | 41.5 |
| 80 | 41.40 | 55.5 | 1.341 | 20.87 | 14.9 | 47 |
| 70 | 34.1 | 63.0 | 1.853 | 26.7 | 10.8 | 50(?) |

The volumes of lower-proof alcohols used by an engine are so large that the fuel pump and carburetor would have to be completely redesigned for normal operation. Fuel tanks would have to be made larger. For example, a tank that would carry a vehicle 200 miles on

gasoline would carry it about 135 miles on anhydrous alcohol (200-proof). The mileage on 120-proof would be 60, that on 90-proof, 40, whereas on 70 proof, the mileage would be less than 25. It is probably that there would be considerable trouble in operation due to wetting of the spark plugs.

There is progressive loss in thermal efficiency as the proof is lowered. Some of this undoubtedly is due to poor distribution, which could be corrected, but a considerable part of it is due to latent heat of vaporization of the water in the blend.

The use of low-proof alcohols as motor fuels is not considered practical whenever facilities for redistillation are available.

### 4. EXHAUST-GAS ANALYSIS IN PART-THROTTLE OPERATION

The percentage of $CO_2$ reached its maximum with all the fuels used in the part-throttle (road-load) tests near the stoichiometric air-fuel ratio. A slight excess of air was indicated at the peak of the curve, but this was less than the range of error in reading of the instruments.

The maximum percentage of $CO_2$ was slightly lower with gasoline than it was when the engine was operated on the alcohol fuels. This may be attributed to at least two possible causes. The theoretical maximum percentage of $CO_2$ is 15.0 with alcohol and 14.9 with gasoline. The alcohol molecule is smaller than that of most of the hydrocarbons that make up gasoline, and it may be possible that there is more complete combustion because the chemical changes that take place are less complex.

D'Alleva and Lovell [3] found that the maximum percentage of $CO_2$ with gasoline generally occurred with a mixture ratio of about 14.7, which is approximately the stoichiometric mixture. However, even with leaner mixtures, there was a small amount of carbon monoxide, and with richer mixtures there was a small amount of oxygen. This may be partly attributed to imperfect distribution and partly to the mechanics of combustion.

According to Gerrish and Voss [4], the carbon monoxide and oxygen may vary from 0 to 9.0 percent. They cite one reference [5] that question the presence of CO in lean mixtures and of oxygen in rich mixtures. Other references [3 and 6] note that there are at least small amounts of both present with any mixture ratio. A study of various types of exhaust-gas analyzers was made by Dilworth in 1941 [7].

Although the theoretical maximum percentage of $CO_2$ is about 14.9 with gasoline, the curve flattens out at a lower point at the top, probably because different cylinders have different individual mixture ratios at any given time, and the engine as a whole never operates at the stoichiometric ratio.

The actual content of $CO_2$ varies from about 9 to about 14 percent, and seems to be independent of the engine speed except in cases accounted for by poor distribution. The maximum percentage of $CO_2$ with 190-proof alcohol when operating at 20 mph was 12.7 and at 50 mph was 14.7. With gasoline the maximum percentage of $CO_2$ was about the same in both cases—13.7 percent. The distribution with gasoline was good at both speeds; with alcohol the distribution was good at 50 mph but was very poor at 20 mph.

It was indicated by the literature mentioned that at lean or rich mixtures the air-fuel ratio may ordinarily be estimated with reasonable accuracy, if the percentage of one or more of the constituents is known. This view is supported by the results of the $CO_2$ analysis in the current series of tests.

Table 7 shows computed data pertinent to the exhaust-gas analysis of the fuels used in these tests. Table 8 is a summary of the results of the $CO_2$ analysis.

TABLE 7.—*Computed mixture ratios, percentage of* $CO_2$ *for various fuels*

| Fuel | Stoichiometric mixture ratio | Theoretical maximum percentage of $CO_2$ | | | |
|---|---|---|---|---|---|
| | | Excess air 0% | Excess air 10% | Excess air 20% | Excess air 33% |
| 190-proof alcohol | 8.32 | 15.0 | 13.5 | 12.3 | 11.0 |
| 200-proof alcohol | 9.00 | 15.0 | 13.5 | 12.3 | 11.0 |
| 20% ether blend | 8.90 | 15.0 | 13.5 | 12.3 | 11.0 |
| Gasoline | 14.7 to 14.8 | 14.9 | 13.4 | 12.2 | 11.0 |

TABLE 8.—*Maximum percentage of* $CO_2$ *in part-throttle operation of 1942 Plymouth*

[Test engine 4]

| Speed | 190-proof alcohol | 200-proof alcohol | 20-percent ether blend | Gasoline |
|---|---|---|---|---|
| mph | | | | |
| 20 | 12.7 | 13.5 | 13.5 | 13.7 |
| 30 | 14.4 | 14.4 | 14.6 | 14.0 |
| 40 | 15.0 | 14.7 | 14.7 | 13.7 |
| 50 | 14.7 | 14.3 | 14.0 | 13.6 |

## 5. COMBUSTION TEMPERATURES AND DISTRIBUTION

The general trends shown by the spark-plug thermocouple temperatures indicate that the mixture distribution is not as good with alcohol as with gasoline. The highest average temperatures occurred when the mixture ratio was near the point at which the engine develops its maximum power. However, there was a considerable spread in the mixture ratios (considering the engine as a whole) at which the highest temperatures occurred in different cylinders. This varied with different fuels and engines, but was always less with gasoline than with any of the other fuels used. Rabezzana and Kalmar in summarizing the results of a series of tests made with this type of spark plug draw the following conclusions:

"1. The spark-plug temperature is directly proportional to the mean combustion temperature and is a function of the mixture ratio.

"2. Variations in temperature are large enough to warrant its use as an index of the mixture ratio.

"3. The location of the peak of the temperature curve has a definite relation to the peak of the power curve."

The results of the current series of tests tend to verify these conclusions in every respect. The analysis of the combustion-temperature-distribution relationship is based on the assumption that the maximum thermocouple temperatures occur at equal values of the mixture ratio in each of the cylinders. A cylinder that is running richer than the

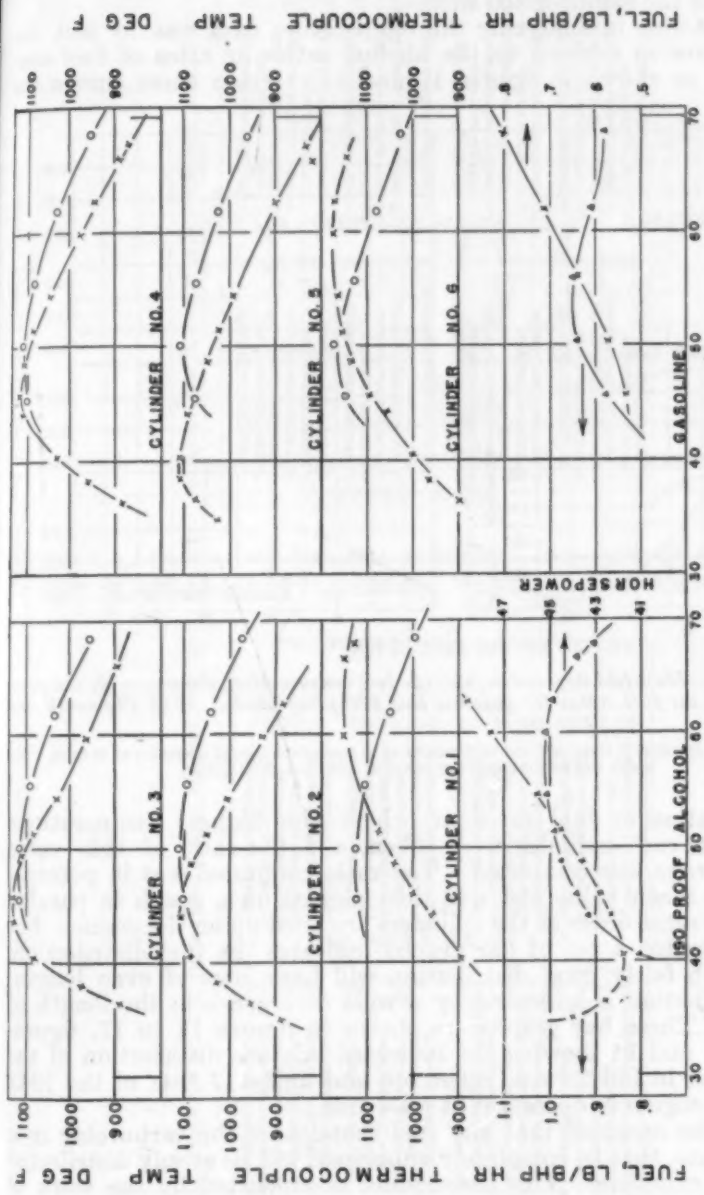


FIGURE 11.—*Power, specific fuel consumption, thermocouple temperatures, and fuel heat input for gasoline and 190-proof alcohol, 1942 Plymouth, test engine 4.*

The engine was operated at 1,500 rpm, full throttle, with spark setting for maximum power. Circles in graphs of cylinder temperatures indicate gasoline, crosses indicate alcohol.

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others will reach its temperature peak when the mixture ratio for the engine as a whole is too lean. Cylinders that receive less than their fair proportion of fuel will reach their highest temperatures when the mixture for the engine is too rich.

The first step in analyzing the temperature data was to plot the temperatures in relation to the air-fuel ratios or rates of fuel consumption, as shown in figures 11 and 12. From these curves the

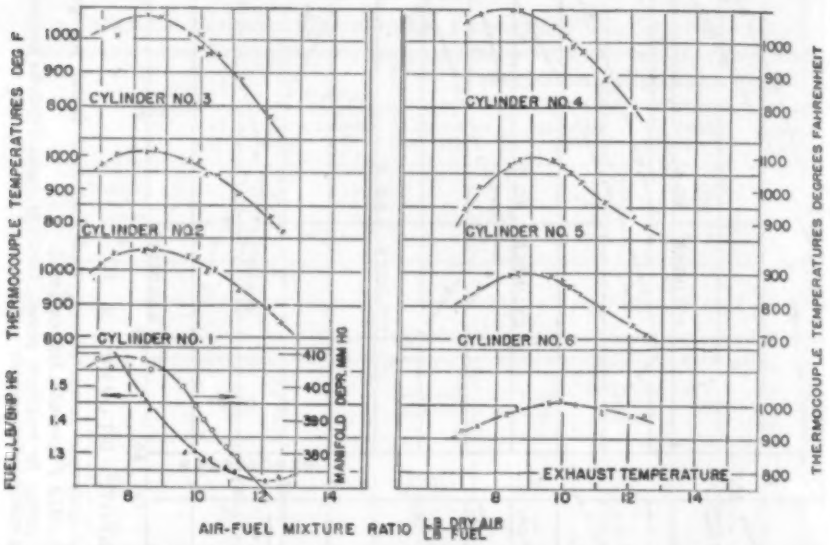


FIGURE 12.—*Manifold depression, specific fuel consumption, thermocouple temperatures, and air-fuel ratios for gasoline and 200-proof alcohol, 1942 Plymouth, test engine 4.*

The engine was operated at the speed and load calculated as equivalent to road operation at 40 mph. The spark was set for maximum power at 1,500 rpm, full throttle.

mixture ratios or fuel rates at which the highest temperatures occurred in each cylinder were taken, and the ratio of this value to the average was computed. The ratio computed was in percentage of the mean value and was then plotted on a graph in parallel bars in the same order as the cylinders are lined up on the engine. For each fuel tested a set of bar graphs indicates the fuel distribution. A fuel with fairly good distribution will have bars of even length; poor distribution is indicated by a wide divergence in the length of the bars. These bar graphs are shown in figures 13 to 17, figures 13, 14, 15, and 16 showing the indicated mixture distribution of the four engines in full-throttle operation and figure 17 that of the 1942 Plymouth engine in operation at road load.

It may be assumed that any fuel that leaves the carburetor in a gaseous state, that is, completely vaporized, will be evenly distributed to all the cylinders. This assumption is supported by the work of Rabezzana and Kalmar [2] on gaseous fuels, using the same type of spark plugs as were used in these tests. With liquid fuels this is true only when the manifold is so designed that each cylinder receives the same amount of unvaporized fuel. Gasoline may be no more than

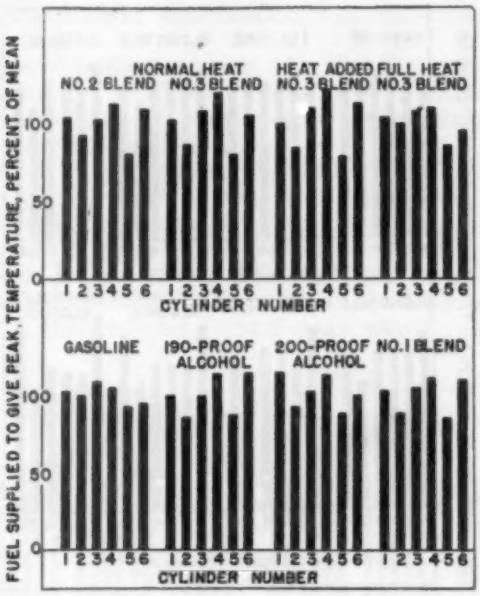
NORMAL HEAT
NO.2 BLEND
NO.3 BLEND
HEAT ADDED
NO.3 BLEND
FULL HEAT
NO.3 BLEND
FUEL SUPPLIED TO GIVE PEAK TEMPERATURE, PERCENT OF MEAN
100
50
0
1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6
CYLINDER NUMBER
GASOLINE
190-PROOF ALCOHOL
200-PROOF ALCOHOL
NO.1 BLEND
100
50
0
1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6
CYLINDER NUMBER

FIGURE 13.—*Mixture distribution with various fuels, 1942 Plymouth, test engine 1*

The engine was operated at 1,500 rpm with full throttle. The spark advance was set for maximum power.

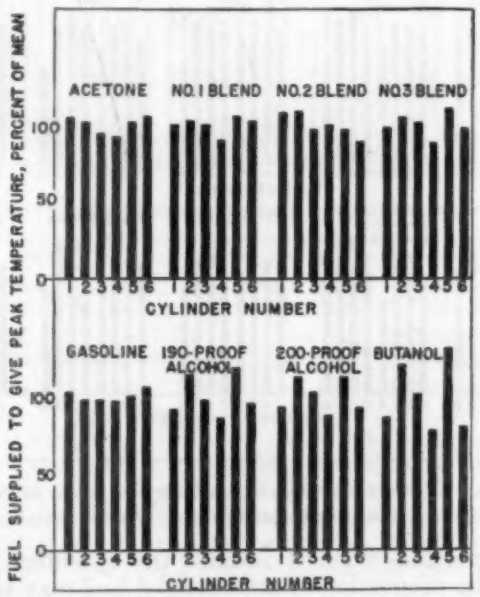
ACETONE
NO.1 BLEND
NO.2 BLEND
NO.3 BLEND
FUEL SUPPLIED TO GIVE PEAK TEMPERATURE, PERCENT OF MEAN
100
50
0
1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6
CYLINDER NUMBER
GASOLINE
190-PROOF ALCOHOL
200-PROOF ALCOHOL
BUTANOL
100
50
0
1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6
CYLINDER NUMBER

FIGURE 14.—*Mixture distribution with various fuels, 1942 Chevrolet.*

The engine was operated at 1,500 rpm with full throttle. The spark advance was set for maximum power.

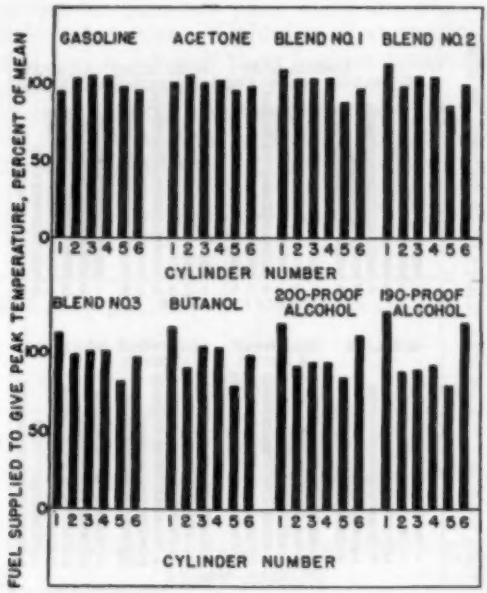


FIGURE 15.—*Mixture distribution with various fuels, 1942 Plymouth, test engine 4.*

The engine was operated at 1,500 rpm with full throttle and spark set for maximum engine power.

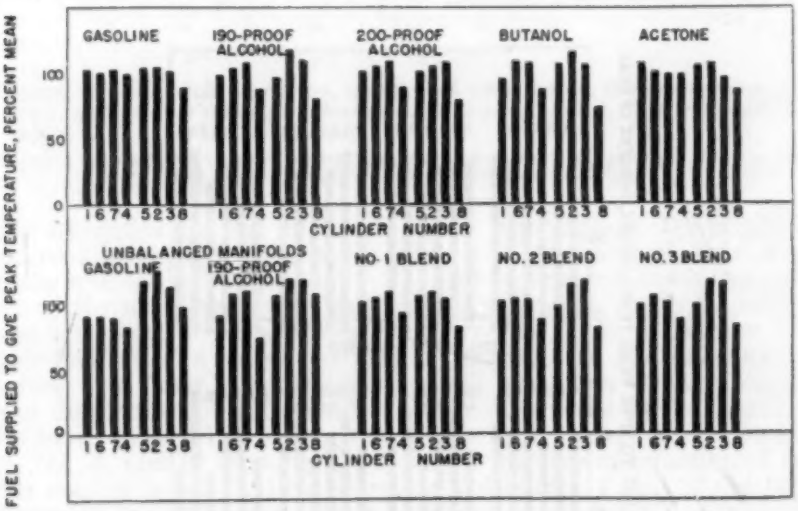


FIGURE 16.—*Mixture distribution, with various fuels, 1940 Ford V–8.*

The engine was operated at 1,500 rpm with full throttle and spark set for maximum engine power.

50 percent vaporized when it reaches the cylinders, and with less volatile fuels the proportion of unvaporized fuel may be even greater. The vaporization takes place throughout the intake manifold and in the cylinder itself during the intake and compression strokes. The rate at which a fuel becomes vaporized depends on its volatility,

boiling point, latent heat of vaporization, and the operating conditions of the engine.

The viscosity and surface tension of a fuel help to determine the path it travels in the manifold. Some of the temperature curves indicate that some of the cylinders received too great a proportion of the fuel added in enrichening a mixture.

The manifold of an automotive engine is built for operation with gasoline. It is to be expected that the other fuels with different physical characteristics would be distributed less uniformly than gasoline. However, there is no reason to believe that it is not possible to build a manifold for any one of these fuels that would distribute the fuel about as well as gasoline is distributed by the present manifold.

It is apparent that several factors may affect fuel distribution.

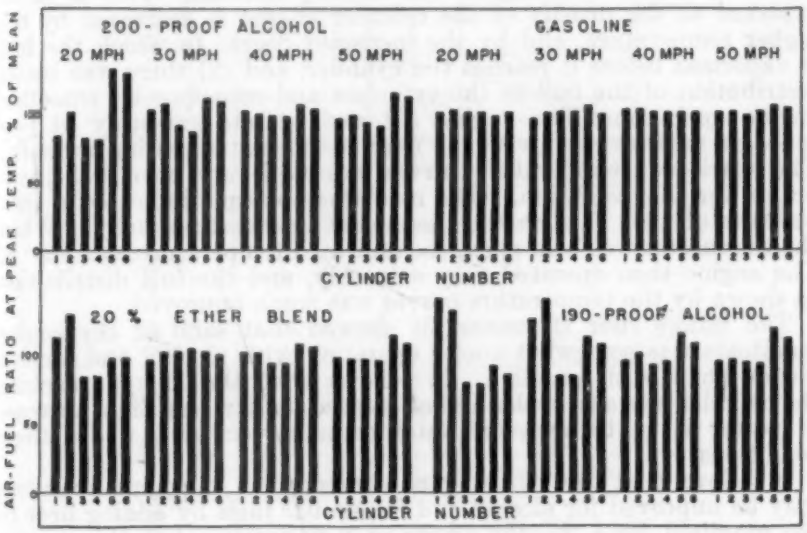


FIGURE 17.—*Mixture ratio distribution with various fuels, 1942 Plymouth, test engine 4.*

The engine was operated at speeds and loads calculated as equivalent to road operation at 20, 30, 40, or 50 mph. The spark was set for maximum power at 1,500 rpm full throttle.

Volatility, viscosity, latent heat of vaporization, and the amount of fuel used are the important factors, but the manner in which they operate is not always consistent. With the Chevrolet engine the end cylinders run slightly leaner than those nearer the carburetor when gasoline is used. With 190- and 200-proof alcohol the end cylinders run richer than the others. With the 1942 Plymouth engine, No. 4, the opposite is true, the middle cylinders being richer with alcohol and leaner with gasoline than are the end cylinders.

Usually, though not always, faults in distribution with gasoline are accentuated when a less volatile fuel is used. In figure 16 it is shown that cylinders No. 4 and No. 8 are somewhat too rich when the Ford engine was operated on gasoline. When the alcohol fuels and blends were used this tendency increased.

With the Ford engine some tests were made in which the dual carburetion system was purposely unbalanced to determine the

effect this would have on the thermocouple temperatures. The cylinders in one manifold group received up to 20 percent more fuel than those in the other group. The temperature peaks of the cylinders in the rich manifold occurred when the other manifold was much too lean for its best performance (see fig. 16).

If vaporization of a fuel improves its distribution by the manifold, any change in operating conditions that increases the rate of vaporization should improve the distribution. The effect of increasing the manifold temperature was studied in tests made with the first Plymouth engine (No. 1).

In some tests of the No. 3 Blend the intake riser thermostat was allowed to operate normally, while in others the thermostat was held open for added heat. The addition of heat had two definite effects: (1) the power of the engine was slightly reduced. This is to be expected as the density of the cylinder charge is decreased by the higher temperature, and by the increased degree to which the fuel is vaporized before it reaches the cylinder, and (2) there was better distribution of the fuel to the cylinders and consequently smoother engine operation. The engine did not operate smoothly at any speed or mixture ratio with the riser thermostat operating normally. The spark-plug temperature curves indicated very poor fuel distribution for this condition. The riser thermocouple indicated a temperature of 193° F when the thermostat operated normally. When the thermostat was held open, the indicated temperature was 420° F. The engine then operated very smoothly, and the fuel distribution as shown by the temperature curves was much improved.

The intake riser thermocouple showed that each of the engine manifolds was somewhat cooler operating with alcohol and alcohol blends than with gasoline. It follows that the charge reaching the cylinder was also cooler and of greater density. A slight increase in power is to be expected (and actually occurred) under these conditions.

It follows that the efficiency and smoothness of engine operation may be improved for alcohol and for similar fuels by adding heat to the manifold for a greater degree of vaporization, but this cannot be accomplished without reducing the maximum power of the engine.

The effect of poor distribution on power and fuel consumption may best be analyzed if the cylinders are considered as independent units, each using its share of the fuel and developing part of the total power of the engine. Tests made on a single-cylinder engine have shown that when the fuel supplied is varied by 10 percent or less from the amount required for maximum power, the power varies 1.1 percent or less from the maximum. Within these limits the effect on engine power of imperfect distribution is less pronounced than that on fuel consumption. A change of 20 percent in the mixture ratio of a cylinder (10 percent rich to 10 percent lean) may be accompanied by a power change of 1 percent or less. With leaner mixtures there may be a sharp drop in engine power without a substantial change in the specific fuel consumption (see fig. 1). The power falls away more sharply with lean than with rich mixtures. For this reason the maximum-power air-fuel ratio always is richer for a multicylinder engine than for a single-cylinder engine operating under similar conditions (see fig. 18). The cylinders that run lean gain more when the mixture is enriched than the other cylinders lose.

A detailed mathematical analysis of the relationship of fuel distribution to power and fuel consumption has been given by Sparrow [8].

The apparent distribution of fuel shown by figures 13 to 16 of this paper may be used to calculate the approximate loss in power due to imperfect distribution, if it is assumed that each cylinder receives its same proportion of fuel throughout the range of air-fuel ratios. It is probable that there is some change in this proportion with changes in air-fuel ratios, but the change is not believed to be large enough to prevent the use of the apparent distribution of the fuel in making estimates of the effects of poor manifolding.

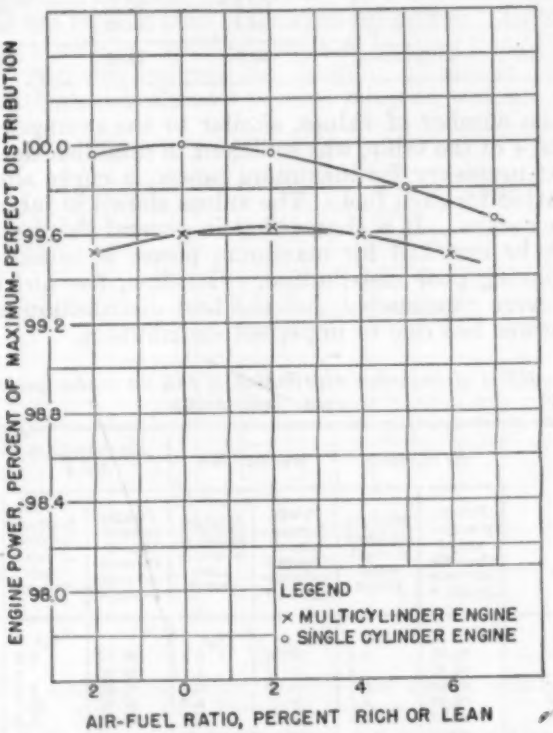


FIGURE 18.—*Effect of imperfect distribution on engine power, 1942 Chevrolet engine, No. 3 Blend.*

The graph is based on an average of the computed power of each of the cylinders in percentage of the theoretical maximum, as shown by tests of a single-cylinder engine. Distribution of fuel is based on figure 14.

A curve was plotted showing the relation of power to fuel consumption in tests of a single-cylinder engine, as shown in figure 18 of reference [1]. This curve was used in estimating the power loss due to imperfect distribution of fuel, as shown by the charts, figures 13 to 16. The percentage of the average amount of fuel received by each cylinder was tabulated, and the power of each cylinder was estimated in percentage of the theoretical maximum, first for the operating condition in which the air-fuel ratio for the whole engine was the same at which a single cylinder developed maximum power, then for various percentages rich or lean, as shown in table 9.

TABLE 9.—*Relation of power to distribution of fuel*

| Cylinder number | Maximum-power mixture ratio | | Fuel-supply increased 2 percent | |
|---|---|---|---|---|
| | Fuel supplied, percentage of average | Single-cylinder power, percentage of potential maximum | Fuel supplied, percentage of requirement for maximum power | Single-cylinder power, percentage of potential maximum |
| 1 | 96.2 | 99.88 | 98.1 | 99.97 |
| 2 | 100.1 | 100.00 | 102.1 | 99.95 |
| 3 | 92.7 | 99.48 | 94.6 | 99.73 |
| 4 | 90.1 | 98.93 | 91.9 | 99.37 |
| 5 | 116.6 | 98.68 | 118.9 | 98.35 |
| 6 | 104.4 | 99.83 | 106.5 | 99.68 |
| Average | 100.0 | 99.47 | 102.0 | 99.51 |

When the number of values, similar to the averages shown in columns 2 and 4 of the table, was sufficient to establish the percentage of enrichment necessary for maximum power, a curve similar to figure 18 was plotted for each fuel. The values shown in table 10 are taken from these curves. It is shown that in general the amount the mixture must be enriched for maximum power is considerably greater for fuels having poor distribution. Gasoline, the fuel for which the manifolds were constructed, has the best distribution and shows the smallest power loss due to imperfect distribution.

TABLE 10.—*Effect of imperfect distribution of fuel on engine performance at 1,500 rpm, full throttle*

| Fuel | 1942 Chevrolet | | 1940 Ford V-8 | | 1942 Plymouth, No. 4 | | 1942 Plymouth, No. 1 | |
|---|---|---|---|---|---|---|---|---|
| | Power, percentage of theoretical maximum [a] | Mixture enriched at maximum power | Power, percentage of theoretical maximum [a] | Mixture enriched at maximum power | Power, percentage of theoretical maximum [a] | Mixture enriched at maximum power | Power, percentage of theoretical maximum [a] | Mixture enriched at maximum power |
| | | %[b] | | %[b] | | %[b] | | %[b] |
| Gasoline | 99.90 | 0.2 | 99.83 | 0.7 | 99.82 | 0.6 | 99.84 | 0.6 |
| Acetone | 99.80 | .4 | 99.70 | 1.1 | 99.92 | .4 | | |
| Butanol | 97.00 | 11.0 | 98.60 | 6.7 | 99.00 | 6.7 | | |
| 190-proof alcohol | 98.86 | 5.7 | 99.07 | 5.0 | 97.83 | 10.7 | 99.08 | 5.1 |
| 200-proof alcohol | 99.02 | 4.0 | 99.34 | 3.7 | 98.86 | 5.5 | 99.29 | 4.2 |
| No. 1 Blend | 99.79 | 1.0 | 99.51 | 3.1 | 99.69 | 2.1 | 99.26 | 3.7 |
| No. 2 Blend | 99.62 | 2.3 | 99.08 | 5.1 | 99.53 | 2.4 | 99.19 | 4.6 |
| No. 3 Blend, intake riser normal | 99.63 | 1.9 | 99.14 | 5.0 | 99.39 | 2.8 | 98.69 | 6.5 |
| No. 3 Blend, heat added | | | | | | | 98.55 | 7.8 |
| No. 3 Blend, full heat on manifold | | | | | | | 99.52 | 2.5 |

[a] Maximum power based on perfect distribution and tests of a single-cylinder engine.
[b] Percentage enriched above maximum power mixture for single-cylinder engine.

## 6. FULL-THROTTLE AIR-FLOW MEASUREMENTS AND MIXTURE RATIOS

The air-flow indicator was not available for use in the full-throttle power and economy tests. However, for the 1942 Plymouth, test engine 4, the air flow could be estimated with reasonable accuracy from measurements made in later tests. With gasoline, 190-proof

alcohol, 200-proof alcohol, and the 20-percent ether blend enough measurements were made to plot curves over the whole range of mixture ratios. For the other fuels similar curves were plotted from air flow estimated by use of available data on gasoline and alcohol under comparable conditions.

The volume of air used by an engine operating at a constant speed and throttle opening varied with different fuels and mixture ratios. The volume reached a minimum when the engine was developing its maximum power and increased up to 3 percent with lean- or rich-mixture ratios. This variation presumably results from the fact that the residual gas and cylinder surfaces are at a maximum temperature when the mixture ratio is that for maximum power. Dilution of the incoming charge with hot residual gas, and heating from the combustion chamber surfaces reduces the amount of charge that can be inducted. With alcohol about 2 percent more air was used than with

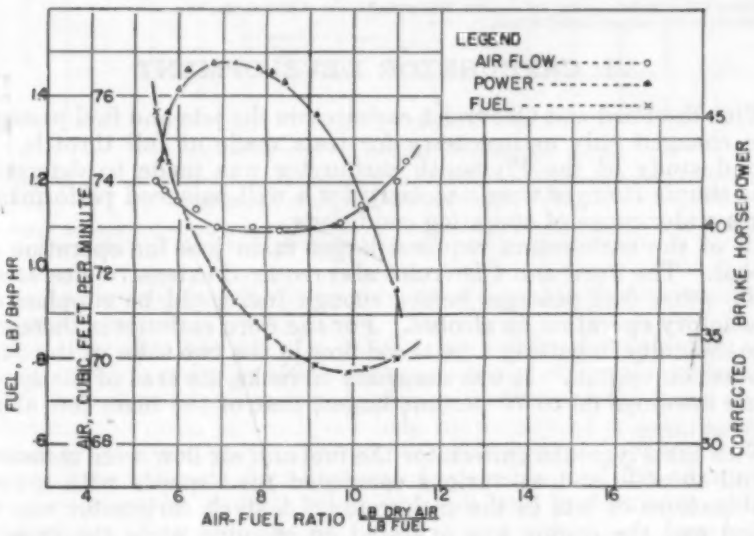


FIGURE 19.—*Fuel consumption, power, air flow, and air-fuel ratio with 200-proof alcohol, 1942 Plymouth, test engine 4.*

The engine was operated at 1,500 rpm, full throttle, with the spark setting for maximum engine power

gasoline at the same engine speed and throttle opening. The increase in volume in this case is probably due to cooler cylinder charges and lower manifold temperatures resulting from the high latent cooling power of the alcohol. Considering the differences in intake manifold temperature and engine power, it is possible to estimate the air flow in full-throttle operation, by comparison of available data on a fuel with data on fuels where the air flow was measured. Figure 19 shows the engine power, fuel consumption, and air flow plotted in relation to the air-fuel ratios when 190-proof alcohol was used at full throttle. Table 11 is a comparison of the performance of the Plymouth engine with various fuels, as shown by curves based on estimated air flow and the measured fuel consumption at 1,500 rpm with full throttle.

TABLE 11.—*Relation of heating values of fuels to mixture ratios and fuel consumption*

[1942 Plymouth. Test engine 4. 1,500 rpm, full-throttle]

| Fuel | Higher heat of combustion | Percentage of heat for gasoline | Mixture ratio at maximum power [b] | Percentage of gasoline maximum power ratio | Mixture ratio at best economy | Percentage of gasoline best economy ratio | Specific fuel consumption | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | lb/bhp hr | Inverse ratio to gasoline used | Direct ratio to gasoline used |
| | *Btu/lb* [a] | | | | | | | | |
| No. 1 blend | 14,380 | 70.8 | 8.4 | 71.2 | 11.0 | 72.3 | 0.602 | 72.3 | 138 |
| No. 2 blend | 14,650 | 72.2 | 8.8 | 74.6 | 11.3 | 74.3 | .680 | 73.5 | 136 |
| No. 3 blend | 14,860 | 73.2 | 9.0 | 76.3 | 11.5 | 75.7 | .660 | 75.8 | 132 |
| Acetone | 13,180 | 64.9 | 7.8 | 66.1 | 9.7 | 63.8 | .770 | 64.9 | 154 |
| Butanol | 15,460 | 76.2 | 9.0 | 76.3 | 11.8 | 77.6 | .645 | 77.5 | 129 |
| 190-proof alcohol | 11,760 | 57.9 | 6.6 | 55.9 | 9.3 | 61.2 | .830 | 60.2 | 166 |
| 200-proof alcohol | 12,720 | 62.6 | 7.0 | 59.3 | 9.8 | 64.5 | .770 | 64.9 | 154 |
| Gasoline | 20,300 | 100 | 11.8 | 100 | 15.2 | 100 | .500 | 100 | 100 |

[a] Higher value as determined by Jessups, National Bureau of Standards, 1943–44.
[b] Pounds of dry air per pound of fuel.

## VI. CARBURETOR DEVELOPMENT

With the Ford and Chevrolet carburetors the jets and fuel passages were changed only as necessary for tests made at full throttle. A limited study of the Plymouth carburetor was made to determine what simple changes were necessary for a well-balanced performance over a wider range of operating conditions.

All of the carburetors required larger main jets for operation on alcohol. The Ford and Chevrolet also required extensive alterations in the other fuel passages before enough fuel could be supplied for satisfactory operation on alcohol. For the Ford carburetor there was some difficulty in getting a balanced flow in the two sides of the dual-carburetion system. It was necessary to make the area of the spray-nozzle openings 60 to 70 percent larger, that of the main jets about twice as large.

With the Plymouth carburetor the fuel and air flow were measured at full throttle and at various computed road speeds with several combinations of jets in the carburetor. A stock carburetor was installed and the engine was operated on gasoline while the rates of flow of air and fuel were measured. The mixture-ratio curve is plotted in relation to road speed in figure 20. The mixture ratio was 12.2 at 20 mph, 14.6 at 30 mph, 15.5 at 40 mph, and 15.6 at 50 mph. This is probably as lean a mixture as can be used without slightly irregular engine performance.

With alcohol several jet sizes were used, but no one jet size would give a well-balanced performance over the whole range of speeds. A 0.075-in. jet gave a satisfactory performance at 40 and 50 mph, but was so lean at lower speeds that it was difficult to keep the engine running. An 0.089-in. jet was satisfactory at full throttle, but gave too rich a mixture at all part-throttle settings, except those at which the idle jet furnished the major part of the fuel supplied. An 0.083-in. jet operated fairly well at all speeds, but was rich at high road speeds, part load, and lean at low speeds and at full throttle. When the idle jet was enlarged in proportion to the main jet, the fuel flow was better balanced but was rich, except at or near full load when the 0.083-in. jet was used. It was indicated that a 0.075-in. jet with an idle tube

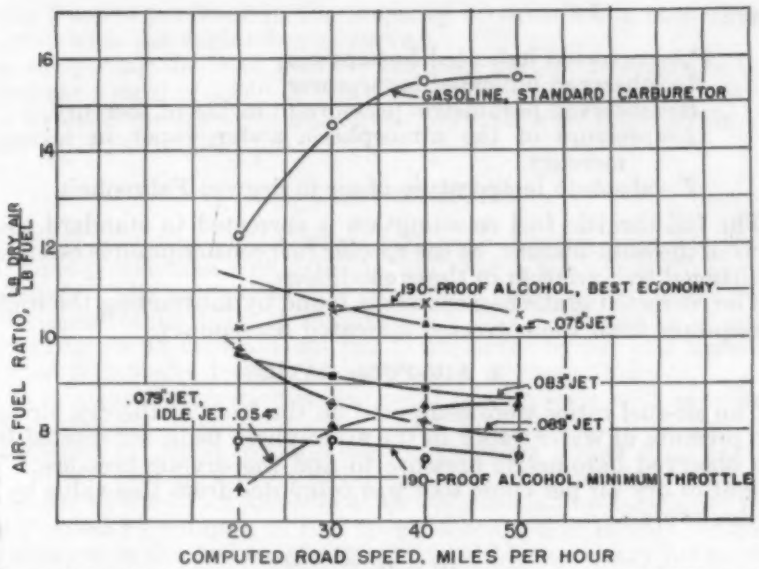


FIGURE 20.—*Carburetor performance and jet sizes with gasoline and 190-proof alcohol, 1942 Plymouth, test engine No. 4.*

The engine was operated at speeds and loads calculated as equivalent to road operation at 20, 30, 40 and 50 mph. The spark was set for maximum power at 1,500 rpm, full throttle.

about 50 percent larger would give an acceptable performance with 190-proof alcohol.

It is clear that the use of a gasoline carburetor for operation with alcohol involves redesign of all basic parts of the carburetor to produce a fuel flow that is proportionately increased in all the basic parts. Enlarging the main jets will not help materially at speeds at which most of the fuel is supplied through the idle passages. Changes of the idle passages will not affect high-speed operation, and the economizer assembly must be altered before the full-load performance will be satisfactory.

## VII. METHODS OF COMPUTING DATA

### 1. FULL-THROTTLE POWER AND FUEL CONSUMPTION

Extensive studies previously made at the National Bureau of Standards [9, 10] have shown that the fuel consumption and indicated horsepower (sum of observed brake and friction horsepower) of an engine operating at constant speed with full throttle vary inversely as the square root of the absolute temperature of the air, and vary directly as the dry-air pressure. In correcting the data, 59° F and 29.53 in. of mercury are taken as standard conditions, and the full-throttle power and fuel consumption are corrected to these conditions by multiplying the observed values by the atmospheric correction factor, as shown by the formula

$$P_c = P_0 \frac{29.53}{B-h} \sqrt{\frac{T}{486.4}},$$

where

$P_c$=corrected indicated horsepower,
$P_0$=observed indicated horsepower,
$B$=observed barometric pressure in inches of mercury,
$h$=pressure of the atmospheric water vapor in inches of mercury,
$T$=absolute temperature of air in degrees Fahrenheit.

The full-throttle fuel consumption is corrected to standard conditions in the same manner, as the specific fuel consumption is essentially unchanged by variation in these conditions.

The corrected brake horsepower is found by subtracting the friction horsepower from the corrected indicated horsepower.

### 2. AIR-FUEL RATIOS

The air-fuel ratios were computed on the basis of the dry air used, the pressure of water vapor in the atmosphere being subtracted from the observed barometric pressure to find the dry-air pressure. The weight of dry air per cubic foot was computed from this value by use of the formula

$$W_1=W_2\frac{(B-h)}{29.92},$$

where

$W_1$=dry air, lb/ft $^3$, at existing atmospheric conditions,
$W_2$=dry air, lb/ft $^3$, at 29.92-in. pressure, existing temperature.

With the weight of air computed on this basis, the mixture ratio was computed as follows:

$$\text{Air, lb/hr}=\text{ft}^3/\text{hr}\times W_1.$$

$$\text{Air-fuel mixture ratio}=\frac{\text{Dry air, lb/hr}}{\text{Fuel, lb/hr}}.$$

### 3. DYNAMOMETER LOAD FOR ROAD-LOAD OPERATION

The load imposed on an automobile engine when propelling a car on a level road is composed of frictional resistance in the power-transmission system, including the tires, and of air resistance to the motion of the car and the rotation of its wheels.

An unpublished study made by Donald B. Brooks, of this Bureau, of the frictional resistance of an automobile shows that the total resistance in level-road operation can be approximated closely by the formula

$$P=0.00000427As^3+0.000000333Ws^2=0.0000333Ws,$$

in which

$P$=horsepower required to propel car,
$A$=projected frontal area of car, ft$^2$,
$W$=weight of car, lb,
$s$=car speed, mph.

Although no formula can represent all cars accurately, because of the differences in the coefficients of air resistance, this formula is a sufficiently good approximation to forecast maximum road speeds

within 2 miles per hour in the majority of cases when used in conjunction with the engine-power curve.

In computing the road load for the 1942 Plymouth engine, a total loaded car weight of 3,860 lb was used. The computed engine speeds used for road speeds of 20, 30, 40, and 50 mph were respectively 935, 1,405, 1,870, and 2,340 rpm.

## VIII. CONCLUSIONS

Engines operating on substitute fuels may develop from 2 to 4 percent more power than with gasoline, but require from 60 to 70 percent more fuel. The amount of any substitute fuel required is inversely proportional to its heat of combustion. The performance of automobile engines on alcohol fuels can be improved by use of a manifold designed specifically for better distribution of these fuels.

The mixture distribution is somewhat less uniform with substitute fuels containing ethyl or normal butyl alcohol than with gasoline. Distribution of highly volatile fuels is generally better than that of those of low volatility, such as butanol or low-proof ethyl alcohol.

The use of low-proof alcohols as motor fuels is impractical because of the excessive volumes of fuel required and other factors. Extensive changes in the fuel supply system would be necessary for normal operation.

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# HEATS, EQUILIBRIUM CONSTANTS, AND FREE ENERGIES OF FORMATION OF THE ACETYLENE HYDROCARBONS THROUGH THE PENTYNES, TO 1,500° K [1]

By Donald D. Wagman, John E. Kilpatrick,[2] Kenneth S. Pitzer,[3] and Frederick D. Rossini

**ABSTRACT**

Values are presented for the following thermodynamic properties for acetylene, propyne (methylacetylene), 1-butyne (ethylacetylene), 2-butyne (dimethylacetylene), 1-pentyne (*n*-propylacetylene), 2-pentyne (methylethylacetylene), and 3-methyl-1-butyne (isopropylacetylene), in the gaseous state, to 1,500° K: The heat-content function, $(H°-H°_0)/T$; the free-energy function, $(F°-H°_0)/T$; the entropy, $S°$; the heat content, $H°-H°_0$; the heat capacity, $C_p°$; the heat of formation from the elements, $\Delta Hf°$; the free energy of formation from the elements, $\Delta Ff°$; and the logarithm of the equilibrium constant of formation from the elements, $\log_{10} Kf$.

Equilibrium constants and concentrations of components are given in tabular and graphical form for the isomerization of the two butynes and of the three pentynes as a function of temperature to 1,500° K. Equilibrium constants are also given in tabular and graphical form for the dehydrogenation of ethane to ethylene to acetylene, of propane to propylene to propyne, of *n*-butane to 1-butene to 1-butyne, and of *n*-pentane to 1-pentene to 1-pentyne.

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[1] This investigation was performed jointly by the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons" and the Thermochemical Laboratory at the National Bureau of Standards.

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## I. INTRODUCTION

As part of the work of the American Petroleum Institute Research Project 44 and the Thermochemical Laboratory at the National Bureau of Standards, values have been calculated for the thermodynamic properties of the heat-content function, free-energy function, entropy, heat content, and heat capacity for the seven acetylene hydrocarbons, $C_2$ to $C_8$, in the gaseous state to 1,500° K. These data have been combined with values of heats of formation at 25° C to calculate values of the heats, free energies, and equilibrium constants of formation of these seven acetylenes, values of the free energies and equilibrium constants of isomerization of the butynes and pentynes, and values of the free energies and equilibrium constants of dehydrogenation, to the corresponding acetylenes, of the $C_2$ to $C_8$ paraffin and olefin hydrocarbons, all to 1,500° K.

## II. UNITS OF ENERGY AND PHYSICAL CONSTANTS

The units of energy, molecular weights, and values of the fundamental constants used in this report are the same as previously described [1].

## III. HEAT-CONTENT FUNCTION, FREE-ENERGY FUNCTION, ENTROPY, HEAT CONTENT, AND HEAT CAPACITY

### 1. METHOD AND DATA USED IN THE CALCULATIONS

Details of the statistical calculations not described here may be found in references [1, 2, 15].*

#### (a) ACETYLENE

The thermodynamic functions of acetylene were computed at each of the tabulated temperatures from the usual translational, rotational, and vibrational terms [1, 2] and from a number of small corrections for the deviation of the acetylene molecule from a rigid rotator-harmonic oscillator. In order to compute these corrections, it was necessary to derive an expression for the rotational-vibrational partition function for a linear molecule. For this purpose, the method of Mayer and Mayer [2] and of Stockmayer, et al [3] was extended as follows:

The energy levels of a linear molecule are given to a good approximation by the relation

$$(\epsilon-\epsilon_0)/kT=\sum_i v_i a_i-\sum_i v_i(v_i-1)Y_{ii}-\sum_{i,j}{}' v_i v_j Y_{ij}+j(j+1)[1-\beta j(j+1)-\sum_i v_i\delta_i]\sigma \quad (1)$$

In the equations the following abbreviations are used:

$\epsilon$ = a given energy level of the molecule,
$\epsilon_0$ = the lowest energy level of the molecule,
$v_i$, $v_j$ = the vibrational quantum numbers of the $i$, $j$, . . . modes of vibration. The subscripts $i$, $j$, $k$ are running indices to distinguish the different modes

*Figures in brackets indicate the literature references at the end of this paper.

of vibration, and each has as many values as the molecule has different frequencies

$j$=a rotational quantum number and is not the same as the vibrational subscript $j$,

$\nu_i$=a fundamental vibrational frequency in wave numbers,

$d_i$=the degeneracy of the $i^{\text{th}}$ fundamental frequency

$u_i=\nu_i hc/kT$,

$X_{ij}$=an anharmonicity coefficient expressed in wave numbers,

$Y_{ij}=X_{ij}hc/kT$ and is a dimensionless anharmonicity coefficient,

$\beta$=a dimensionless rotational stretching coefficient,[4]

$\delta_i$=a dimensionless rotational-vibrational coupling coefficient,

$\sigma=B_0hc/kT$,

$B_0=h/8\pi^2Ic$ and is the rotational line-spacing constant,[4]

$\binom{v_i+d_i-1}{v_i}$=the $v_i$ binominal coefficient of the $(v_i+d_i-1)$ order,

$I$=the moment of inertia of the molecule,

$h$=Planck's constant,

$c$=the velocity of light,

$k$=Boltzmann's constant,

$T$=the absolute temperature.

The above notation follows that of Mayer and Mayer [2].

The energy-level expression is written in terms of the observed fundamentals rather than the zeroth order frequencies because (a) the fundamentals include the first-order effect of anharmonicity, and therefore this correction is reduced, (b) any future change in the anharmonicity coefficients $X_{ij}$ will alter only a small portion of the calculations, and (c) degeneracy enters the equations in a simpler manner.

The azimuthal quantum numbers were not included because they have a negligible effect on the thermodynamic properties.

In the above notation the internal partition function is then

$$Q_{vjm}=\sum_{v_i=0}^{\infty}\cdots\sum_{v_n=0}^{\infty}\sum_{j=0}^{\infty}(2j+1)\left[\prod_i\binom{v_i+d_i-1}{v_i}\right]\exp\left\{-\sum_i v_iu_i+\right.$$

$$\left.\sum_i v_i(v_i-1)Y_{ii}+\sum_{i,k}{}'v_iv_kY_{ik}+j(j+1)[1-\beta j(j+1)-\sum_i v_i\delta_i]\sigma\right\} \tag{2}$$

Summing and neglecting second-order terms,

$$Q_{vjm}=[\prod_i(1-e^{-u_i})^{-d_i}]\sigma^{-1}\left[1+\sum_{i,j}f_{ij}+\sum_i\frac{d_i\delta_i}{e^{u_i}-1}+\frac{2\beta}{\sigma}+\frac{\sigma}{3}\right], \tag{3}$$

where

$$f_{ii}=d_i(d_i+1)Y_{ii}(\exp(u_i)-1)^{-2},$$

$$f_{ij}=d_id_jY_{ij}(\exp(u_i)-1)^{-1}(\exp(u_j)-1)^{-1}.$$

[4] In the notation of Mayer and Mayer [2],

$$\beta=4\gamma^3=D/B_0$$

$$\delta_i=a_i/B_0$$

The usual Einstein functions arise from the first factor. The second factor leads to the rigid rotor rotational terms. The last factor includes the first-order corrections for anharmonicity, rotational-vibrational coupling, rotational stretching, and the first Euler-Maclaurin series summation correction term.

The effect of the correction terms on the thermodynamic properties was calculated by a combination of analytical and graphical methods.

The molecular constants selected for the acetylene molecule are given in table 1. The anharmonicity coefficients were fitted, largely by least squares, to Wu's [4] assignment of the harmonics and combination bands. The anharmonicity coefficients involving frequencies $\nu_1$, $\nu_2$, and $\nu_3$ are based on many observed lines and have little uncertainty, whereas those involving $\nu_4$ and $\nu_5$ are considerably more uncertain. However, the coefficients selected reproduce satisfactorily the observed lines in the spectrum of acetylene. The remaining constants and coefficients in table 1 were taken from Mecke [5].

TABLE 1.—*Molecular constants selected for the acetylene molecule*

Fundamental vibration frequencies, in wave numbers, $cm^{-1}$:

| | | | |
|---|---|---|---|
| C≡C stretching | $\nu_1$ | = | 1973 |
| C—H stretching, unsymmetrical | $\nu_2$ | = | 3372 |
| C—H stretching, symmetrical | $\nu_3$ | = | 3288 |
| Bending | $\nu_4$ | = | 729 |
| Do | $\nu_5$ | = | 612 |

Anharmonicity coefficients, $X_{ij}$, in wave numbers, $cm^{-1}$:

| $j$ \ $i$= | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 1 | 12 | 5 | 5 | −2.5 | 10 |
| 2 | 5 | 49 | 73 | 5 | 5 |
| 3 | 5 | 73 | 5 | 5 | 5 |
| 4 | −2.5 | 5 | 5 | 0 | −2.5 |
| 5 | 10 | 5 | 5 | −2.5 | −5 |

Moment of inertia constants:

$$B_0 = h/8\pi^2 cI = 1.1764 \text{ cm}^{-1},$$
$$I = 23.7895 \times 10^{-40} \text{ g cm}^2.$$

Rotational stretching coefficient:

$$\beta = 1.556 \times 10^{-6}.$$

Rotational-vibrational interaction coefficients:

| | |
|---|---|
| Stretching | $\delta_1 = \delta_2 = \delta_3 = -0.00434$, |
| Bending | $\delta_4 = \delta_5 = 0.0017$. |

Table 2 gives the numerical values of the corrections (I, II, III, and IV) to the thermodynamic properties of the heat-content function, the free-energy function, and the heat capacity that are to be applied to the values calculated for the acetylene molecule on the basis of a rigid rotator—simple harmonic oscillator. Correction I arises from the actual anharmonicity of the vibrations. Correction II arises from the coupling between vibration and rotation. Correction III arises from the increase in moment of inertia with the rotational quantum number, $j$, and is referred to as the rotational stretching effect. Correction IV arises from the use of the integral in place of actual summation over the rotational energy levels and is important only in molecules having a small moment of inertia.

#### (b) PROPYNE (METHYLACETYLENE)

The value selected for the larger moment of inertia of methylacetylene was $98.276\times10^{-40}$ g cm$^2$, derived from the mean of the values of $B_0$ reported by Herzberg, et al [6], 0.28458 cm$^{-1}$, and by Badger and Bauer [7], 0.28496 cm$^{-1}$. This value of the moment of inertia and the values of 1.060, 1.11, and 1.207 angstrom units for the lengths of the acetylenic C—H, the methyl C—H, and the acetylenic C≡C, bonds, respectively, yield 1.462 angstrom units for the length of the C—C single bond in methylacetylene. The smaller moment of inertia then has the value $5.499\times10^{-40}$ g cm$^2$. The symmetry number is 3.

The entropy of translation and rotation for methylacetylene in the ideal gaseous standard state is

$$S^\circ_{t+r}=10.417+18.3026\log_{10}T \text{ cal/deg mole.}$$

The vibrational frequencies selected for methylacetylene are, in wave numbers, cm$^{-1}$

| | |
|---|---|
| 926 | 333 (2) |
| 1,380 | 642 (2) |
| 2,151 | 1,041 (2) |
| 2,910 | 1,444 (2) |
| 3,380 | 2,995 (2) |

This assignment of frequencies is that of Crawford [9], with the exception that 3,380 is used in place of the value 3,430 recommended by Crawford for the acetylenic C—H stretching motion. The lower value was obtained from an unpublished infrared spectrogram [16] and is supported by the value 3,300 obtained for the same vibration from the Raman spectrum of the liquid [11].

#### (c) 1-BUTYNE (ETHYLACETYLENE)

The following values were selected for the lengths of the bonds in the ethylacetylene molecule: Acetylenic C—H, 1.060; acetylenic C≡C, 1.207; ≡C—C<, 1.462; paraffinic C—C, 1.54; methylene C—H, 1.11; methyl C—H, 1.09, angstrom units. The product of the external moments of inertia is $1{,}164.5\times10^{-117}$ (g cm$^2$)$^3$. The reduced internal moment of inertia is $4.847\times10^{-40}$ g cm$^2$.

For ethylacetylene in the ideal gaseous standard state, the entropy of translation, rotation, and free internal rotation is

$$S^\circ_{t+r+fr}=14.407+20.5904\log_{10}T \text{ cal/deg mole.} \quad (5)$$

TABLE 2.—*Values of the correction terms to the rigid-rotator–harmonic oscillator approximation for the thermodynamic functions of acetylene*

[For the explanation of I, II, III, IV, see text.]

| Temperature | Corrections to heat-content function in cal/deg. mole | | | | Corrections to free-energy function in cal/deg mole | | | | Corrections to heat capacity in cal/deg mole | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | I | II | III | IV | I | II | III | IV |
| °K | | | | | | | | | | | | |
| 298.16 | −0.0066 | +0.0000 | +0.0011 | −0.0038 | +0.0012 | −0.0005 | −0.0011 | −0.0038 | −0.0347 | +0.0000 | +0.0022 | 0 |
| 300 | −.0067 | .0000 | .0011 | −.0038 | .0013 | −.0005 | −.0011 | −.0038 | −.0352 | .0000 | .0022 | 0 |
| 400 | −.0186 | .0003 | .0015 | −.0028 | .0047 | −.0014 | −.0015 | −.0028 | −.0760 | .0002 | .0029 | 0 |
| 500 | −.0345 | .0008 | .0018 | −.0023 | .0106 | −.0024 | −.0018 | −.0023 | −.1177 | .0006 | .0037 | 0 |
| 600 | −.0511 | .0014 | .0022 | −.0019 | .0184 | −.0035 | −.0022 | −.0019 | −.1519 | .0012 | .0044 | 0 |
| 700 | −.0676 | .0022 | .0026 | −.0016 | .0276 | −.0046 | −.0026 | −.0016 | −.1800 | .0021 | .0051 | 0 |
| 800 | −.0831 | .0030 | .0029 | −.0014 | .0377 | −.0057 | −.0029 | −.0014 | −.2018 | .0032 | .0059 | 0 |
| 900 | −.0972 | .0039 | .0033 | −.0012 | .0483 | −.0068 | −.0033 | −.0012 | −.2188 | .0045 | .0066 | 0 |
| 1,000 | −.1099 | .0049 | .0037 | −.0011 | .0592 | −.0079 | −.0037 | −.0011 | −.2317 | .0061 | .0073 | 0 |
| 1,100 | −.1213 | .0060 | .0040 | −.0010 | .0703 | −.0089 | −.0040 | −.0010 | −.2410 | .0078 | .0081 | 0 |
| 1,200 | −.1314 | .0071 | .0044 | −.0009 | .0813 | −.0099 | −.0044 | −.0009 | −.2470 | .0096 | .0088 | 0 |
| 1,300 | −.1403 | .0083 | .0047 | −.0009 | .0921 | −.0110 | −.0047 | −.0009 | −.2500 | .0114 | .0095 | 0 |
| 1,400 | −.1481 | .0094 | .0051 | −.0008 | .1028 | −.0119 | −.0051 | −.0008 | −.2512 | .0133 | .0103 | 0 |
| 1,500 | −.1550 | .0105 | .0055 | −.0007 | .1133 | −.0129 | −.0055 | −.0007 | −.2519 | .0152 | .0110 | 0 |

No assignment of frequencies for ethylacetylene has been published. This molecule has 24 internal degrees of freedom, as follows: 9 valence stretching vibrations; 14 deformation, or bending, vibrations; and 1 hindered rotation. The selection rules permit all these frequencies to be active in both Raman and infrared spectra. The assignment of frequencies was made on the basis of the Raman spectrum [12] and the infrared spectrum [28] by means of a normal coordinate calculation and by analogy to the assignments of methylacetylene [9] and propane [13] and by comparison with the Raman spectra of other monosubstituted acetylenes [12]. The resulting assignment of frequencies follows, in wave numbers, $cm^{-1}$:

| *Stretching modes* | | *Bending modes* | |
|---|---|---|---|
| H−C≡ | 3380 | H−C≡C | 642 |
| C≡C | 2151 | H−C≡C | 642 |
| C−C≡ | 840 | C≡C−C | 206 |
| C−C | 1068 | C≡C−C | 348 |
| | 2963 | C−C−C | 509 |
| $CH_2$ | 2963 | | 784 |
| and | 2963 | | 1005 |
| $CH_3$ | 2963 | | 1252 |
| | 2963 | $CH_2$ | 1252 |
| | | and | 1314 |
| | | $CH_3$ | 1456 |
| | | | 1375 |
| | | | 1438 |
| | | | 1459 |

No experimental data on heat capacity or the entropy of the gas are available for evaluating the barrier hindering internal rotation. As the structural relations in this respect resemble those of ethane more than any other molecule, the same barrier has been used as in ethane, 2,710 cal/mole [17]. The contribution of the hindered internal rotation to the respective thermodynamic properties was evaluated from the tables of Pitzer and Gwinn [15].

### (d) 2-BUTYNE (DIMETHYLACETYLENE)

It has been known for some time that the values of the heat capacity and entropy of gaseous dimethylacetylene calculated statistically from the usually accepted spectroscopic and molecular data can not be made to agree well with both the heat capacity and the entropy determined experimentally. Statistical calculations involving (a) appropriate dimensions from methylacetylene, with the length of the C−H bond in the methyl groups taken as 1.09 angstrom units, and (b) Crawford's assignment of frequencies [10], with free internal rotation, yield values of heat capacity in accord with those determined experimentally by Kistiakowsky and Rice [11], but a value of the entropy at the normal boiling point, which is 0.4 cal/degree mole lower than the value determined calorimetrically by Osborne, Garner, and Yost [14]. Assumption of hindered rotation of the methyl groups could only lower the statistically calculated value of the entropy, which is already too low, and, furthermore, would raise the statistically calculated heat capacities above the experimentally determined values. No important change appears permissible in the lengths of the C−C and C≡C bonds, which have been determined with satisfactory accord from electron-diffraction measurements for methylacetylene and dimethylacetylene [8], and from spectroscopic measurements for

methylacetylene [6, 7]. The assignment of frequencies made by Crawford [9] appears to be satisfactory, as he has shown that the same potential constants reproduce the spectra of acetylene, methylacetylene, and dimethylacetylene.

In order to improve the situation slightly, two minor changes have been made in the present investigation, with regard to the molecular constants of dimethylacetylene, as follows:

(a) The length of the C—H bond in the methyl group is taken as 1.11 angstrom units, in place of the usually accepted value of 1.09 angstrom units. Justification for this change is that the stretching frequencies associated with the C—H bonds were calculated by Crawford [9, 10], using potential constants taken from ethane, to be lower than those actually observed. By the application of Badger's rule [29], this could mean that the lengths of the C—H bonds in methylacetylene and dimethylacetylene are a little greater than 1.09 angstrom units. This change is even more justified because of the fact that the value of 1.11 angstrom units for the length of the C—H bond in the methyl group leads to a value of the moment of inertia ($5.499\times10^{-40}$ g cm$^2$), which is in essentially exact accord with the values of the moment of inertia of the methyl group determined spectroscopically for ethane and each of the four methyl halides [30].

(b) The lowest frequency is changed from 213 to 209 wave numbers, cm$^{-1}$. Justification for this change is that the lowest frequency in dimethylacetylene, which is that associated with the symmetrical bending of the carbon skeleton, has been observed only in the Raman spectrum of the liquid, and the frequency of a vibration measured in the liquid phase is often several wave numbers, cm$^{-1}$, different from the frequency of the same vibration measured in the gaseous phase.

The two foregoing changes produce substantially no change in the statistically calculated values of the heat capacity but reduce the difference between the statistically calculated and experimentally determined values of the entropy from 0.4 to 0.2 cal/deg mole, which is near the uncertainty of the experimentally determined value.

On the basis of the foregoing changes, the molecular constants for dimethylacetylene are taken as follows:

Moments of inertia, $249.84\times10^{-40}$ and $10.998\times10^{-40}$g cm$^2$; reduced moment of inertia for internal rotation, $2.750\times10^{-40}$g cm$^2$; symmetry number, 18; frequencies,

| | | | |
|---|---|---|---|
| 725 | 1126 | 209 (2) | 371 (2) |
| 1380 | 1380 | 1050 (2) | 1029 (2) |
| 2270 | 2976 | 1468 (2) | 1448 (2) |
| 2916 | | 2976 (2) | 2966 (2) |

For dimethylacetylene in the ideal gaseous standard state, the entropy of translation and rotation, including free internal rotation, is

$$S^\circ_{t+r+fr}=9.758+20.5904\log_{10}T \text{ cal/deg mole} \quad (6)$$

### (c) THE THREE PENTYNES

As neither calorimetric data nor complete spectroscopic data for any of the pentynes were available, an approximate method of calculation was used for these molecules, involving the addition to the values for 1-butyne of contributions arising from appropriate structural increments determined from the lower members of the paraffin and acetylene series. The values of the heat-content function, free-energy function, and heat capacity were determined in this manner. From these values the entropies and heat contents were calculated.

For 1-pentyne (*n*-propylacetylene) the values were calculated to be those for 1-butyne (ethylacetylene) plus the difference between the values for *n*-butane and propane. No correction in the free-energy function due to symmetry number is necessary.

For 2-pentyne (methylethylacetylene) the values were calculated to be those for 1-butyne plus the difference between 2-butyne (dimethylacetylene) and propyne (methylacetylene). The free-energy function is decreased by $R\ln 2$ because of the difference in the symmetry numbers of 2-butyne and propyne.

For 3-methyl-1-butyne (isopropylacetylene), the values were calculated to be those for 1-butyne plus the difference between isobutane and propane. The free-energy function is decreased by $R\ln 3/2$ because of the difference in the symmetry numbers of isobutane and propane.

The required values for 2-butyne and propyne were taken from the calculations of this report, and the values for propane, *n*-butane, and isobutane were taken from Pitzer [17] and from some unpublished calculations [18].

## 2. RESULTS FOR THE SEVEN ACETYLENE HYDROCARBONS, $C_2$ TO $C_5$

The resulting values of the thermodynamic properties for the seven acetylene hydrocarbons through the pentynes are given in tables 3, 4, 5, 6, and 7, which give, respectively, values of the heat-content function, $(H^\circ-H_0^\circ)/T$, the free-energy function, $(F^\circ-H_0^\circ)/T$, the entropy, $S^\circ$, the heat content, $H^\circ-H_0^\circ$, and the heat capacity, $C_p^\circ$.

The values given in tables 3, 4, 5, 6, and 7 may be compared with previously published values as follows:

(a) Values of the free-energy function for acetylene were reported by Gordon [19] and by Kassel [20]. Gordon's values for the free-energy function at 298.16° and 1,000° K, corrected to the new values of the fundamental physical constants [1], are −39.980 and −52.127 cal/deg mole, respectively, as compared with the values −39.976 and −52.005 cal/deg mole, respectively, as given in table 4.

(b) Values of the heat capacity of methylacetylene and of dimethylacetylene in the gaseous state were determined experimentally by Kistiakowsky and Rice [11]. A comparison of these data with the appropriate values from table 7, obtained by Lagrangian four-point interpolation [21], is shown in table 8. The accord is very satisfactory.

TABLE 3.—*Values*[a] *of the heat content function,* $(H°-H_0°)/T$, *for the seven acetylene hydrocarbons,* $C_2$ *to* $C_8$, *for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature ° K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Heat-content function,[b] $(H°-H_0°)/T$, in cal/deg mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 0 | 8.021 | 8.036 | 8.853 | 9.582 | 10.212 | 10.762 | 11.249 | 11.689 | 12.090 | 12.460 | 12.802 | 13.119 | 13.416 | 13.694 |
| Propyne (methylacetylene) | $C_3H_4$ | 0 | 10.41 | 10.44 | 11.82 | 13.17 | 14.44 | 15.62 | 16.72 | 17.73 | 18.67 | 19.54 | 20.35 | 21.10 | 21.80 | 22.45 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 0 | 12.81 | 12.83 | 15.08 | 17.22 | 19.22 | 21.09 | 22.80 | 24.38 | 25.83 | 27.18 | 28.42 | 29.58 | 30.65 | 31.64 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 0 | 13.28 | 13.32 | 15.15 | 17.03 | 18.86 | 20.62 | 22.28 | 23.84 | 25.29 | 26.64 | 27.90 | 29.06 | 30.15 | 31.16 |
| 1-Pentyne | $C_5H_8$ | 0 | 16.61 | 16.64 | 19.6 | 22.4 | 25.1 | 27.5 | 29.8 | 31.8 | 33.7 | 35.5 | 37.1 | 38.7 | 40.1 | 41.4 |
| 2-Pentyne | $C_5H_8$ | 0 | 15.68 | 15.72 | 18.4 | 21.1 | 23.6 | 26.1 | 28.4 | 30.5 | 32.4 | 34.3 | 36.0 | 37.5 | 39.0 | 40.4 |
| 3-Methyl-1-butyne | $C_5H_8$ | 0 | 15.37 | 15.40 | 18.6 | 21.6 | 24.5 | 27.0 | 29.4 | 31.5 | 33.5 | 35.3 | 37.0 | 38.5 | 39.9 | 41.2 |

[a] Interpolation to other temperatures in the interval 298.16° to 1,500° K may be made by appropriate graphical or analytical methods. For temperatures between 200° and 298.16° K, values may be estimated by extrapolating the values for 300°, 400°, 500°, and 600° K. The values in this table are given to more significant figures than are warranted by the absolute accuracy of the individual values in order to retain the internal consistency of the several thermodynamic functions of a single substance, and also to retain the significance of the increments with temperature of a given thermodynamic function.

[b] The heat content function, $(H°-H_0°/T)$, is the heat content at the given temperature less the heat content at 0° K, divided by the absolute temperature (° K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atm).

TABLE 4.—*Values*[a] *of the free energy function,* $(F°-H_0°)/T$, *for the seven acetylene hydrocarbons,* $C_2$ *to* $C_8$, *for the ideal gaseous state, to 1,500° K*

TABLE 4.—*Values*[a] *of the free energy function,* $(F^\circ - H_0^\circ)/T$, *for the seven acetylene hydrocarbons,* $C_2$ *to* $C_8$, *for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature in °K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Free energy function,[b] $(F^\circ - H_0^\circ)/T$, in cal/deg mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 0 | −39.976 | −40.025 | −42.451 | −44.508 | −46.313 | −47.930 | −49.400 | −50.752 | −52.005 | −53.175 | −54.275 | −55.313 | −56.296 | −57.231 |
| Propyne (methylacetylene) | $C_3H_4$ | 0 | −48.89 | −48.95 | −52.14 | −54.92 | −57.44 | −59.76 | −61.91 | −63.94 | −65.86 | −67.68 | −69.42 | −71.07 | −72.66 | −74.19 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 0 | −56.70 | −56.78 | −60.78 | −64.38 | −67.70 | −70.81 | −73.74 | −76.51 | −79.16 | −81.69 | −84.11 | −86.43 | −88.66 | −90.81 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 0 | −54.43 | −54.51 | −58.89 | −62.18 | −65.44 | −68.48 | −71.35 | −74.06 | −76.65 | −79.12 | −81.50 | −83.78 | −85.97 | −88.09 |
| 1-Pentyne | $C_5H_8$ | 0 | −62.49 | −62.60 | −67.8 | −72.5 | −76.8 | −80.9 | −84.7 | −88.3 | −91.8 | −95.1 | −98.2 | −101.2 | −104.2 | −107.0 |
| 2-Pentyne | $C_5H_8$ | 0 | −63.62 | −63.72 | −68.6 | −73.0 | −77.1 | −80.9 | −84.5 | −88.0 | −91.3 | −94.5 | −97.6 | −100.5 | −103.3 | −106.1 |
| 3-Methyl-1-butyne | $C_5H_8$ | 0 | −60.86 | −60.95 | −65.8 | −70.3 | −74.5 | −78.5 | −82.2 | −85.8 | −89.2 | −92.5 | −95.6 | −98.7 | −101.6 | −104.4 |

[a] See footnote a of table 3.

[b] The free energy function, $(F^\circ - H_0^\circ)/T$, is the free energy at the given temperature less the heat content at 0°K, divided by the absolute temperature (°K), of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atm).

TABLE 5.—*Values[a] of the entropy, $S°$, for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature in °K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Entropy,[b] $S°$, in cal/deg mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 0 | 47.997 | 48.061 | 51.304 | 54.090 | 56.525 | 58.692 | 60.649 | 62.441 | 64.095 | 65.635 | 67.077 | 68.432 | 69.712 | 70.925 |
| Propyne (methylacetylene) | $C_3H_4$ | 0 | 59.30 | 59.39 | 63.96 | 68.09 | 71.88 | 75.38 | 78.63 | 81.67 | 84.53 | 87.22 | 89.77 | 92.17 | 94.46 | 96.64 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 0 | 69.51 | 69.61 | 75.86 | 81.60 | 86.92 | 91.90 | 96.54 | 100.89 | 104.99 | 108.87 | 112.53 | 116.01 | 119.31 | 122.45 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 0 | 67.71 | 67.83 | 73.74 | 79.21 | 84.30 | 89.10 | 93.63 | 97.90 | 101.94 | 105.76 | 109.40 | 112.84 | 116.12 | 119.25 |
| 1-Pentyne | $C_5H_8$ | 0 | 79.10 | 79.24 | 87.4 | 94.9 | 101.9 | 108.4 | 114.5 | 120.1 | 125.5 | 130.6 | 135.3 | 139.9 | 144.3 | 148.4 |
| 2-Pentyne | $C_5H_8$ | 0 | 79.30 | 79.44 | 87.0 | 94.1 | 100.7 | 107.0 | 112.9 | 118.5 | 123.7 | 128.8 | 133.6 | 138.0 | 142.3 | 146.5 |
| 3-Methyl-1-butyne | $C_5H_8$ | 0 | 76.23 | 76.35 | 84.4 | 91.9 | 99.0 | 105.5 | 111.6 | 117.3 | 122.7 | 127.8 | 132.6 | 137.2 | 141.5 | 145.6 |

[a] See footnote a of table 3.
[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atm).

TABLE 6.—*Values[a] of the heat content ($H° - H_0°$) for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

TABLE 6.—*Values* [a] *of the heat content* $(H^\circ - H_0^\circ)$ *for the seven acetylene hydrocarbons,* $C_2$ *to* $C_8$, *for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature in °K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Heat content,[b] $(H^\circ - H_0^\circ)$ in cal/mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 0 | 2391.5 | 2410.8 | 3541.2 | 4791.0 | 6127 | 7533 | 8999 | 10520 | 12090 | 13706 | 15362 | 17055 | 18782 | 20541 |
| Propyne (methylacetylene) | $C_3H_4$ | 0 | 3104 | 3131 | 4728 | 6584 | 8663 | 10935 | 13372 | 15956 | 18670 | 21490 | 24420 | 27430 | 30520 | 33670 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 0 | 3820 | 3850 | 6031 | 8610 | 11540 | 14760 | 18240 | 21940 | 25830 | 29890 | 34110 | 38450 | 42910 | 47460 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 0 | 3961 | 3995 | 6060 | 8513 | 11320 | 14440 | 17830 | 21450 | 25290 | 29300 | 33480 | 37780 | 42210 | 46740 |
| 1-Pentyne | $C_5H_8$ | 0 | 4952 | 4992 | 7840 | 11210 | 15000 | 19300 | 23800 | 28700 | 33700 | 39100 | 44600 | 50300 | 56100 | 62100 |
| 2-Pentyne | $C_5H_8$ | 0 | 4675 | 4716 | 7360 | 10540 | 14200 | 18300 | 22700 | 27400 | 32500 | 37700 | 43200 | 48800 | 54600 | 60500 |
| 3-Methyl-1-butyne | $C_5H_8$ | 0 | 4583 | 4620 | 7440 | 10820 | 14700 | 18900 | 23500 | 28400 | 33500 | 38800 | 44400 | 50100 | 55900 | 61900 |

[a] See footnote a of table 3.

[b] $(H^\circ - H_0^\circ)$ is the heat content at the given temperature less the heat content at 0° K of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atm.).

TABLE 7.—*Values* [a] *of the heat capacity, $C_p°$, for the seven acetylene hydrocarbons, $C_2$ to $C_5$, for the ideal gaseous state, to 1,500° K*

| Compound (gas) | For-mula | Temperature in °K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Heat capacity, [b] $C_p°$, in cal/deg mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 0 | 10.490 | 10.532 | 11.973 | 12.967 | 13.728 | 14.306 | 14.933 | 15.449 | 15.922 | 16.353 | 16.744 | 17.069 | 17.418 | 17.704 |
| Propyne (methylacetylene) | $C_3H_4$ | 0 | 14.50 | 14.55 | 17.33 | 19.74 | 21.80 | 23.53 | 25.14 | 26.51 | 27.71 | 28.77 | 29.69 | 30.50 | 31.21 | 31.84 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 0 | 19.46 | 19.54 | 23.87 | 27.63 | 30.83 | 33.57 | 35.93 | 38.02 | 39.84 | 41.42 | 42.80 | 44.01 | 45.06 | 45.98 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 0 | 18.63 | 18.70 | 22.62 | 26.36 | 29.68 | 32.50 | 35.14 | 37.36 | 39.29 | 40.98 | 42.44 | 43.71 | 44.82 | 45.78 |
| 1-Pentyne | $C_5H_8$ | 0 | 25.50 | 25.65 | 31.1 | 36.1 | 40.4 | 44.0 | 47.1 | 49.8 | 52.2 | 54.3 | 56.1 | 57.7 | 59.1 | 60.2 |
| 2-Pentyne | $C_5H_8$ | 0 | 23.59 | 23.69 | 29.2 | 34.3 | 38.7 | 42.6 | 45.9 | 48.9 | 51.4 | 53.6 | 55.6 | 57.2 | 58.7 | 59.9 |
| 3-Methyl-1-butyne | $C_5H_8$ | 0 | 25.02 | 25.13 | 31.1 | 36.2 | 40.6 | 44.2 | 47.4 | 50.1 | 52.4 | 54.5 | 56.3 | 57.8 | 59.2 | 60.4 |

[a] See footnote a of table 3.

[b] $C_p°$ is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atm).

TABLE 8.—*Comparison of observed and calculated gas heat capacities for methylacetylene and dimethylacetylene*

| Propyne (methylacetylene) | | | 2-Butyne (dimethylacetylene) | | |
|---|---|---|---|---|---|
| $T$ | $C_p°$ (obs.) | $C_p°$ (calc.) | $T$ | $C_p°$ (obs.) | $C_p°$ (calc.) |
| °K | *cal/deg mole* | *cal/deg mole* | °K | *cal/deg mole* | *cal/deg mole* |
| 272.28 | 13.76 | 13.71 | 336.07 | 20.21 | 20.12 |
| 299.59 | 14.58 | 14.54 | 369.46 | 21.43 | 21.43 |
| 332.83 | 15.56 | 15.50 | | | |
| 369.21 | 16.52 | 16.51 | | | |

(c) A value for the entropy of dimethylacetylene in the gaseous state at 291° K was determined experimentally by Osborne, Garner, and Yost [14] by application of the third law of thermodynamics to calorimetric measurements down to 15° K. Extrapolation to 291.00° K of the values of entropy for dimethylacetylene given in table 5 yields the value 67.27 cal/deg mole, which is to be compared with the value 67.48 ±0.20 cal/deg mole from the experimental data of Yost and coworkers.

(d) Values of the free-energy function, entropy, and heat capacity, of gaseous methylacetylene were calculated by Crawford [9]. Crawford's values for the free-energy function at 298.16° and 1,000° K, corrected to the new values of the fundamental physical constants [1] are −48.85 and −65.81 cal/deg mole, respectively, as compared with the values −48.89 and −65.86 cal/deg mole, respectively, as given in table 4. See also Frank-Kamenetzky and Markovich [22].

## IV. HEAT OF FORMATION, FREE ENERGY OF FORMATION, AND EQUILIBRIUM CONSTANT OF FORMATION

### 1. METHOD AND DATA USED IN THE CALCULATIONS

The same method of calculation was used as described in Section IV–1 of reference [1].

For the heats of formation of the seven acetylene hydrocarbons, $C_2$ to $C_5$, in the gaseous state at 25° C, according to the reaction

$$nC \text{ (solid, graphite)} + (n-1)H_2(\text{gas}) = C_nH_{2n-2}(\text{gas}), \qquad (7)$$

with each reactant and product in its standard state, the following values were used [23]: Acetylene, 54.194 ±0.190; propyne (methylacetylene), 44.319 ±0.207; 1-butyne (ethylacetylene), 39.70 ±0.50; 2-butyne (dimethylacetylene), 35.374 ±0.350; 1-pentyne, 34.50 ± 0.50; 2-pentyne, 30.80 ±0.50; 3-methyl-1-butyne, 32.60 ±0.50 kcal/mole.

### 2. RESULTS FOR THE SEVEN ACETYLENE HYDROCARBONS, $C_2$ TO $C_5$

The resulting values of the thermodynamic properties for the formation of the seven acetylene hydrocarbons, $C_2$ to $C_5$, in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gaseous), are presented in tables 9, 10, and 11, which give, respectively, values of the heat of formation, $\Delta Hf°$, the free energy of formation, $\Delta Ff°$, and the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, all to 1,500° K.

TABLE 9.—*Values* [a] *of the heat of formation, $\triangle Hf°$, for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature in ° K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Heat of formation,[b] $\triangle Hf°$, in kcal/mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 54.329 | 54.194 | 54.193 | 54.134 | 54.049 | 53.931 | 53.787 | 53.627 | 53.462 | 53.304 | 53.151 | 53.003 | 52.851 | 52.698 | 52.548 |
| Propyne (methylacetylene) | $C_3H_4$ | 46.017 | 44.319 | 44.309 | 43.775 | 43.280 | 42.829 | 42.423 | 42.069 | 41.769 | 41.53 | 41.34 | 41.19 | 41.06 | 40.95 | 40.86 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 42.96 | 39.70 | 39.68 | 38.79 | 38.00 | 37.32 | 36.74 | 36.26 | 35.88 | 35.60 | 35.39 | 35.27 | 35.17 | 35.12 | 35.08 |
| 2-Butyne (Dimethylacetylene) | $C_4H_6$ | 38.491 | 35.374 | 35.355 | 34.348 | 33.432 | 32.63 | 31.95 | 31.38 | 30.92 | 30.59 | 30.33 | 30.17 | 30.03 | 29.95 | 29.89 |
| 1-Pentyne | $C_5H_8$ | 38.90 | 34.50 | 34.47 | 33.31 | 32.28 | 31.44 | 30.73 | 30.16 | 29.72 | 29.40 | 29.21 | 29.11 | 29.09 | 29.10 | 29.13 |
| 2-Pentyne | $C_5H_8$ | 35.48 | 30.80 | 30.77 | 29.41 | 28.20 | 27.17 | 26.30 | 25.62 | 25.07 | 24.69 | 24.44 | 24.28 | 24.19 | 24.16 | 24.17 |
| 3-Methyl-1-butyne | $C_5H_8$ | 37.37 | 32.60 | 32.57 | 31.37 | 30.37 | 29.55 | 28.84 | 28.30 | 27.89 | 27.60 | 27.44 | 27.37 | 27.36 | 27.37 | 27.38 |

[a] See footnote (a) of table 3.

[b] $\triangle Hf°$ represents the increment in heat content for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 10.—*Values* [a] *of the free energy of formation, $\triangle Ff°$, for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

TABLE 10.—*Values* [a] *of the free energy of formation, $\Delta Ff°$, for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

| Compound (gas) | Formula | Temperature in °K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Free energy of formation,[b] $\Delta Ff°$, in kcal/mole | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | 54.329 | 50.000 | 49.975 | 48.577 | 47.196 | 45.835 | 44.498 | 43.178 | 41.882 | 40.604 | 39.339 | 38.089 | 36.854 | 35.624 | 34.410 |
| Propyne (methylacetylene) | $C_3H_4$ | 46.017 | 46.313 | 46.481 | 47.267 | 48.224 | 49.255 | 50.360 | 51.514 | 52.715 | 53.95 | 55.20 | 56.46 | 57.74 | 59.02 | 60.32 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | 42.96 | 48.52 | 48.57 | 51.67 | 54.99 | 58.45 | 62.02 | 65.66 | 69.36 | 73.10 | 76.85 | 80.62 | 84.41 | 88.20 | 91.99 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | 38.491 | 44.725 | 44.783 | 48.080 | 51.620 | 55.34 | 59.18 | 63.10 | 67.10 | 71.14 | 75.20 | 79.29 | 83.39 | 87.49 | 91.60 |
| 1-Pentyne | $C_5H_8$ | 38.90 | 50.17 | 50.26 | 55.71 | 61.42 | 67.33 | 73.38 | 79.50 | 85.69 | 91.92 | 98.17 | 104.46 | 110.78 | 117.06 | 123.31 |
| 2-Pentyne | $C_5H_8$ | 35.48 | 46.41 | 46.51 | 51.96 | 57.74 | 63.75 | 69.92 | 76.19 | 82.55 | 88.96 | 95.39 | 101.84 | 108.32 | 114.79 | 121.26 |
| 3-Methyl-1-butyne | $C_5H_8$ | 37.37 | 49.12 | 49.23 | 54.96 | 60.97 | 67.17 | 73.50 | 79.92 | 86.40 | 92.93 | 99.47 | 106.04 | 112.61 | 119.15 | 125.68 |

[a] See footnote a of table 3.

[b] $\Delta Ff°$ represents the increment in free energy for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

TABLE 11.—*Values* [a] *of the logarithm of the equilibrium constant of formation, $\log_{10} Kf$, for the seven acetylene hydrocarbons, $C_2$ to $C_8$, for the ideal gaseous state, to 1,500° K*

| Compound | Formula | Temperature in ° K | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | | Logarithm of equilibrium constant of formation,[b] $\log_{10} Kf$ | | | | | | | | | | | | | | |
| Ethyne (acetylene) | $C_2H_2$ | Infinite | −36.6490 | −36.4058 | −26.5406 | −20.6290 | −16.6952 | −13.8925 | −11.7978 | −10.1702 | −8.8738 | −7.8158 | −6.9369 | −6.1956 | −5.5611 | −5.0134 |
| Propyne (methylacetylene) | $C_3H_4$ | ...do... | −33.9469 | −33.8610 | −25.8360 | −21.0781 | −17.9409 | −15.7228 | −14.0728 | −12.8007 | −11.7897 | −10.9660 | −10.2830 | −9.7072 | −9.2137 | −8.7879 |
| 1-Butyne (ethylacetylene) | $C_4H_6$ | ...do... | −35.5616 | −35.3839 | −28.2320 | −24.0341 | −21.2892 | −19.3627 | −17.9369 | −16.8427 | −15.9748 | −15.2680 | −14.6832 | −14.1910 | −13.7682 | −13.4030 |
| 2-Butyne (dimethylacetylene) | $C_4H_6$ | ...do... | −32.7823 | −32.6236 | −26.2690 | −22.5629 | −20.1556 | −18.4752 | −17.2380 | −16.2932 | −15.5471 | −14.9409 | −14.4400 | −14.0186 | −13.6574 | −13.3462 |
| 1-Pentyne | $C_5H_8$ | ...do... | −36.7712 | −36.6154 | −30.4369 | −26.8440 | −24.5230 | −22.9082 | −21.7167 | −20.8084 | −20.0881 | −19.5046 | −19.0244 | −18.6227 | −18.2733 | −17.9662 |
| 2-Pentyne | $C_5H_8$ | ...do... | −34.0177 | −33.8792 | −28.3891 | −25.2377 | −23.2205 | −21.8297 | −20.8130 | −20.0457 | −19.4412 | −18.9519 | −18.5480 | −18.2095 | −17.9186 | −17.6668 |
| 3-Methyl-1-butyne | $C_5H_8$ | ...do... | −36.0061 | −35.8614 | −30.0293 | −26.6495 | −24.4662 | −22.9486 | −21.8318 | −20.9810 | −20.3088 | −19.7622 | −19.3118 | −18.9315 | −18.6004 | −18.3115 |

[a] See footnote (a) of table 3.

[b] $\log_{10} Kf$ represents the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound in the gaseous state from the elements carbon (solid, graphite) and hydrogen (gaseous), with all the reactants and products in their appropriate standard reference states at the temperature indicated.

Figure 1 shows the thermodynamic stability of the four 1-alkynes in the gaseous state as a function of temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with corresponding plots for the normal paraffins and the 1-alkenes, which are given in other reports from this laboratory [24, 25].

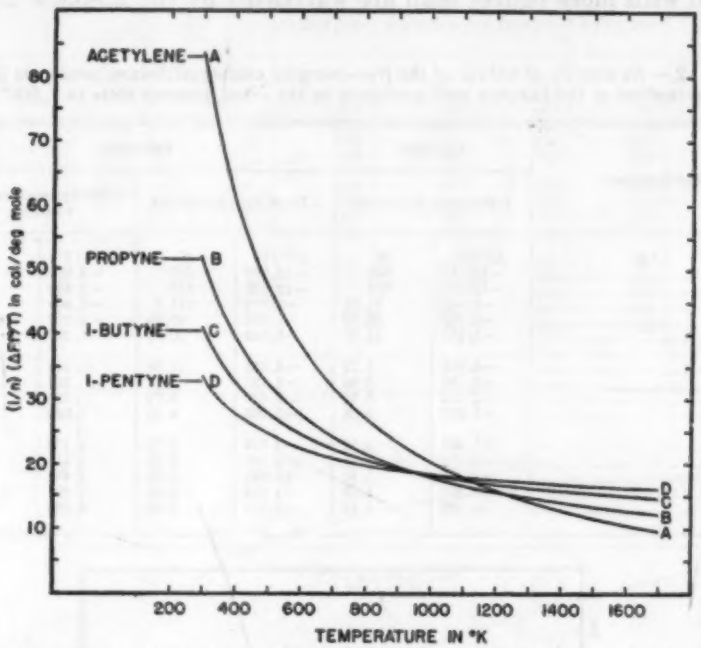


FIGURE 1.—*Thermodynamic stability of the 1-alkyne hydrocarbons in the gaseous state as a function of temperature.*

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff°/T)$ in calories per degree mole, where $n$ is the number of carbon atoms per molecule, $T$ is the absolute temperature in degrees Kelvin, and $\Delta Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, as given in table 10. The scale of abscissas gives the temperature in degrees Kelvin. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid carbon (graphite) and gaseous hydrogen in their respective standard states.

## V. FREE ENERGIES AND EQUILIBRIUM CONSTANTS OF ISOMERIZATION OF THE BUTYNES AND THE PENTYNES

From the values in tables 10 and 11, calculations were made of the values of the free energies, equilibrium constants, and equilibrium concentrations for the isomerization of the butynes and pentynes, according to the reaction.

$$C_nH_{2n-2}\ (\text{1-alkyne, gas}) = C_nH_{2n-2}\ (\text{isomeric alkyne, gas}).$$

In table 12 are given the following:

$\Delta F°/T$, the standard free-energy change divided by the absolute temperature, for the isomerization reaction as written; $K$, the equilibrium constant, for the isomerization reaction as written. In table 13 are given values of $N$, the mole fraction of the given isomer present

at equilibrium with its other isomers (acetylene compounds). For any two isomers, the ratio of the corresponding values of $K$ in table 12 (or of $N$ in table 13) gives the ratio of the amounts of those two isomers present at equilibrium with one another in the gas phase at the given temperature. For the purpose of retaining the significance of their change with temperature, the values in tables 12 and 13 are written with more figures than are warranted by the absolute uncertainty.

TABLE 12.—*Summary of values of the free-energies and equilibrium constants for the isomerization of the butynes and pentynes in the ideal gaseous state to 1,500° K*

| Temperature | Butynes | | Pentynes | | | |
|---|---|---|---|---|---|---|
| | 1-Butyne=2-butyne | | 1-Pentyne=2-pentyne | | 1-Pentyne=3-methyl-1-butyne | |
| °K | $\Delta F°/T$ | $K$ | $\Delta F°/T$ | $K$ | $\Delta F°/T$ | $K$ |
| 298.16 | −12.717 | 602 | −12.599 | 567 | −3.501 | 5.82 |
| 300 | −12.630 | 576 | −12.580 | 545 | −3.450 | 5.68 |
| 400 | −8.982 | 91.84 | −9.370 | 111.6 | −1.865 | 2.56 |
| 500 | −6.732 | 29.59 | −7.350 | 40.39 | −0.890 | 1.56 |
| 600 | −5.187 | 13.60 | −5.900 | 20.07 | −.260 | 1.14 |
| 700 | −4.061 | 7.72 | −4.935 | 11.98 | +.185 | 0.91 |
| 800 | −3.198 | 5.00 | −4.135 | 8.01 | . .527 | .77 |
| 900 | −2.514 | 3.54 | −3.490 | 5.79 | .790 | .67 |
| 1,000 | −1.957 | 2.68 | −2.960 | 4.44 | 1.010 | .60 |
| 1,100 | −1.497 | 2.12 | −2.529 | 3.57 | 1.179 | .55 |
| 1,200 | −1.113 | 1.75 | −2.180 | 3.00 | 1.315 | .52 |
| 1,300 | −0.789 | 1.49 | −1.891 | 2.59 | 1.413 | .49 |
| 1,400 | −.507 | 1.29 | −1.623 | 2.26 | 1.497 | .47 |
| 1,500 | −.260 | 1.14 | −1.370 | 1.99 | 1.580 | .45 |

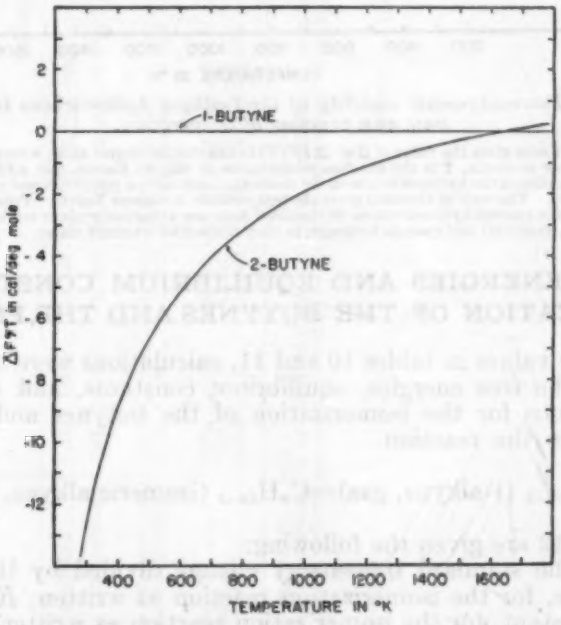


FIGURE 2.—*Free energy of isomerization of the butynes.*

The scale of ordinates gives the value of $\Delta F°/T$, in calories per degree mole, for the isomerization of 1-butyne (gas) into 2-butyne (gas). The scale of abscissas gives the temperature in degrees Kelvin.

TABLE 13.—*Values of the equilibrium concentrations for the isomerization of the butynes and pentynes in the ideal gaseous state to 1,500° K*

| Temperature | Composition, in mole fraction, of equilibrium mixtures of isomers | | | | |
|---|---|---|---|---|---|
| | Butynes | | Pentynes | | |
| | 1-Butyne | 2-Butyne | 1-Pentyne | 2-Pentyne | 3-Methyl-1-butyne |
| °K | | | | | |
| 298.16 | 0.002 | 0.998 | 0.002 | 0.988 | 0.010 |
| 300 | .002 | .998 | .002 | .988 | .010 |
| 400 | .011 | .989 | .009 | .969 | .022 |
| 500 | .033 | .967 | .023 | .941 | .036 |
| 600 | .068 | .932 | .045 | .903 | .052 |
| 700 | .115 | .885 | .072 | .863 | .065 |
| 800 | .167 | .833 | .102 | .820 | .078 |
| 900 | .220 | .780 | .134 | .776 | .090 |
| 1,000 | .272 | .728 | .166 | .734 | .100 |
| 1,100 | .320 | .680 | .195 | .697 | .108 |
| 1,200 | .364 | .636 | .222 | .664 | .114 |
| 1,300 | .402 | .598 | .245 | .635 | .120 |
| 1,400 | .436 | .564 | .268 | .606 | .126 |
| 1,500 | .467 | .533 | .290 | .579 | .131 |

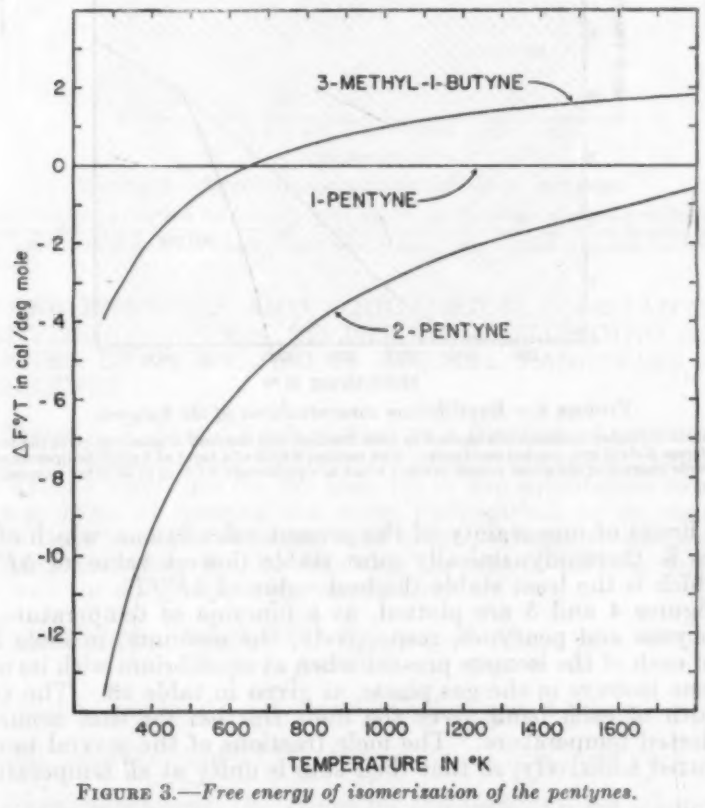


FIGURE 3.—*Free energy of isomerization of the pentynes.*

The scale of ordinates gives the value of $\Delta F°/T$, in calories per degree mole, for the isomerization of 1-pentyne (gas) into the appropriate isomeric pentyne (gas). The scale of abscisssas gives the temperature in degrees Kelvin.

In figures 2 and 3 are plotted, as a function of the temperature, the values of $\Delta F°/T$ given in table 12 for the isomerization of the butynes and the pentynes, respectively. These plots may be compared with corresponding plots for the butanes, pentanes, hexanes, heptanes, and octanes, which have already been published [26, 27], and for the butenes, pentenes, and hexenes, which will appear in another report from this laboratory [25]. From these charts one may see at a glance, for any temperature in the given range and with-

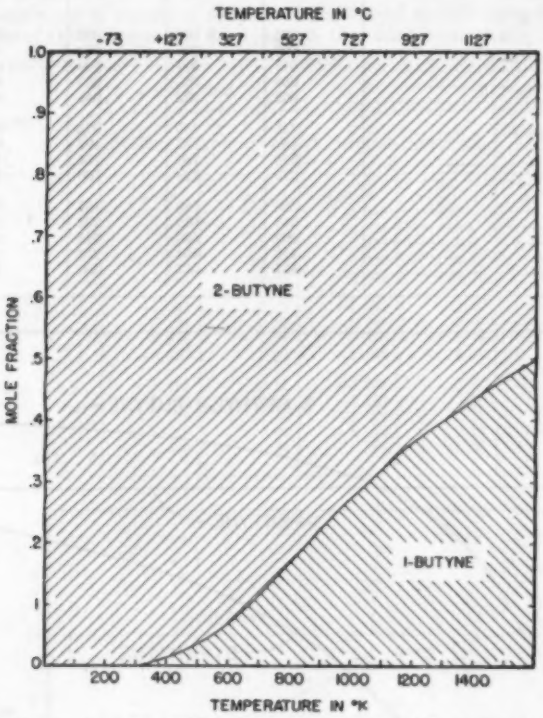


FIGURE 4.—*Equilibrium concentrations of the butynes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

in the limits of uncertainty of the present calculations, which of the isomers is thermodynamically most stable (lowest value of $\Delta F°/T$) and which is the least stable (highest value of $\Delta F°/T$).

In figures 4 and 5 are plotted, as a function of temperature, for the butynes and pentynes, respectively, the amounts, in mole fraction, of each of the isomers present when at equilibrium with its other acetylene isomers in the gas phase, as given in table 13. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

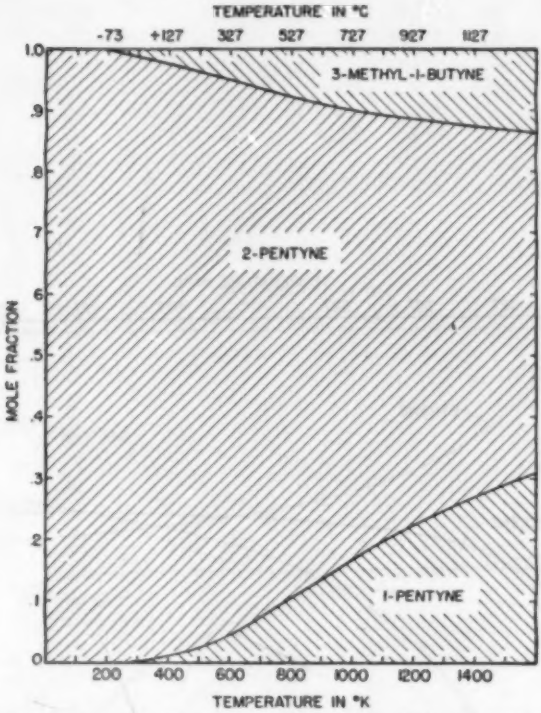


FIGURE 5.—*Equilibrium concentrations of the pentynes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

## VI. FREE ENERGIES AND EQUILIBRIUM CONSTANTS OF DEHYDROGENATION, TO THE CORRESPONDING ACETYLENES, OF THE $C_2$ TO $C_5$ NORMAL PARAFFINS AND 1-ALKENES

In figures 6, 7, 8, and 9 are plotted as a function of temperature, for the $C_2$, $C_3$, $C_4$, and $C_5$ hydrocarbons, respectively, values of $\log_{10} Kf$, the logarithm (to the base 10) of the equilibrium constant of the reaction of forming the given hydrocarbon in its standard gaseous state from the elements solid carbon (graphite) and gaseous hydrogen, according to the following equations for the paraffin, olefin, and the acetylene series, respectively:

$$n\text{C (solid, graphite)} + (n+1)\ \text{H}_2\ \text{(gas)} = \text{C}_n\text{H}_{2n+2}\ \text{(gas, normal paraffin)} \quad (9)$$

$$n\text{C (solid, graphite)} + n\text{H}_2\ \text{(gas)} = \text{C}_n\text{H}_{2n}\ \text{(gas, 1-alkene)} \quad (10)$$

$$n\text{C (solid, graphite)} + (n-1)\ \text{H}_2\ \text{(gas)} = \text{C}_n\text{H}_{2n-2}\ \text{(gas, 1-alkyne)}. \quad (11)$$

In these calculations, the values for the 1-alkynes are taken from this report, the values for the normal paraffins from reference [24], and those for the 1-alkenes from reference [25].

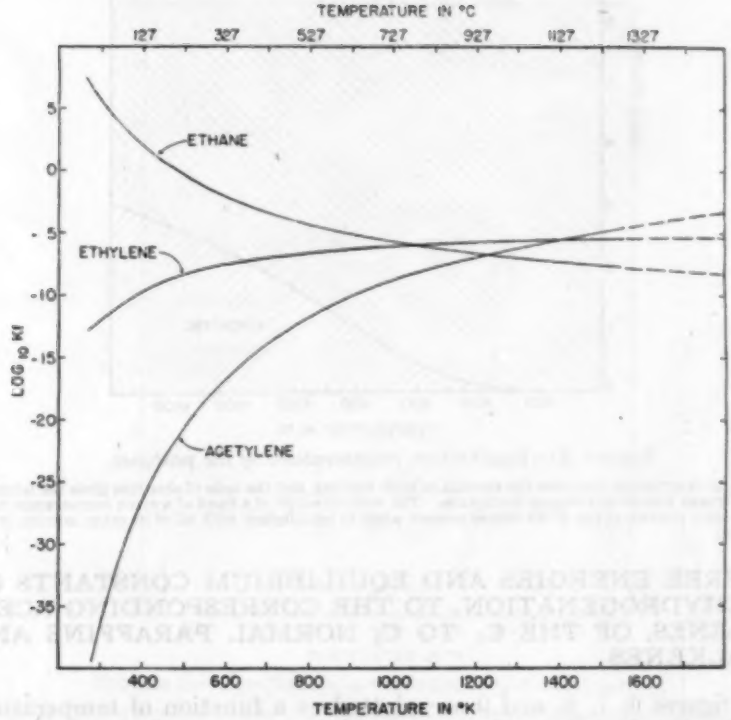


FIGURE 6.—*Logarithm of the equilibrium constant of formation of ethane, ethylene, and acetylene.*

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons in the gaseous state from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. (See text.)

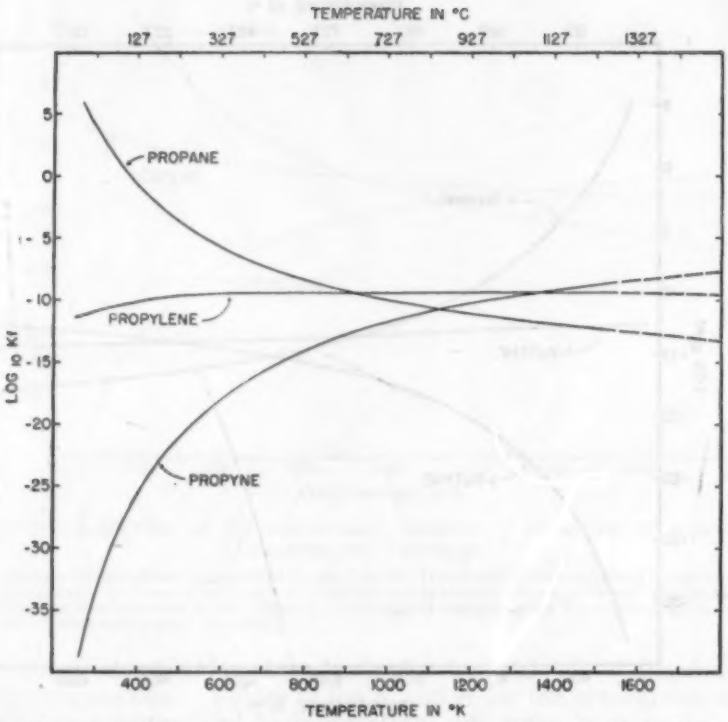


FIGURE 7.—*Logarithm of the equilibrium constant of formation of propane, propylene, and propyne.*

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. (See text.)

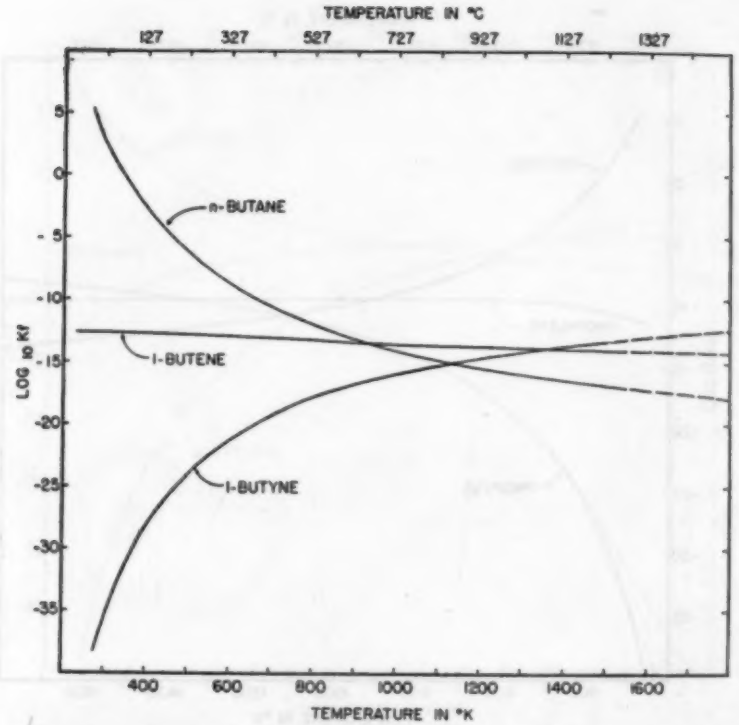


FIGURE 8.—*Logarithm of the equilibrium constant of formation of n-butane, 1-butene, and 1-butyne.*

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. (See text.)

The differences in the values of the ordinates of any given pair of curves in figures 6, 7, 8, and 9 give the values of the logarithm of the

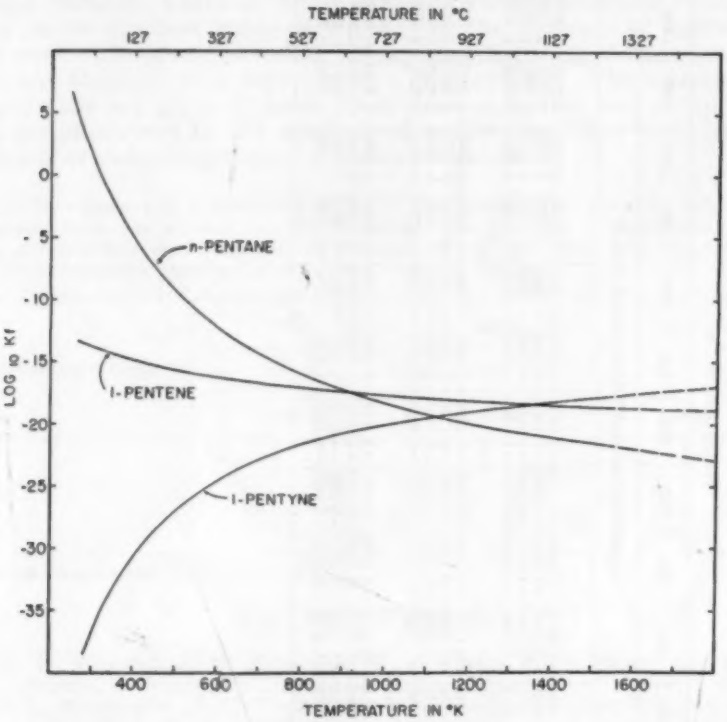


FIGURE 9.—*Logarithm of the equilibrium constant of formation of n-pentane, 1-pentene, and 1-pentyne.*

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. (See text.)

equilibrium constant for the appropriate reaction of hydrogenation or dehydrogenation. Values of log $K$ and $K$ for the several reactions of dehydrogenation (and hydrogenation) are given in table 14.

TABLE 14.—*Logarithm of the equilibrium constant for the dehydrogenation reactions involving n-paraffins, 1-alkenes and 1-alkynes, $C_2$ to $C_5$*

| Reaction | Temperature in °K | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.16 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1,000 | 1,100 | 1,200 | 1,300 | 1,400 | 1,500 |
| | Logarithm of the equilibrium constant, log $_{10}K$ | | | | | | | | | | | | | |
| n-Paraffin (gas) = 1-alkene (gas) + $H_2$(gas): | | | | | | | | | | | | | | |
| $C_2H_6$(gas) = $C_2H_4$(gas) + $H_2$(gas) | −17.6958 | −17.5494 | −11.5404 | −7.9014 | −5.4444 | −3.6778 | −2.3423 | −1.2992 | −0.4684 | +0.2229 | 0.7937 | 1.2706 | 1.6897 | 2.0496 |
| $C_3H_8$(gas) = $C_3H_6$(ra) + $H_2$(gas) | −16.0835 | −14.9822 | −9.4934 | −6.1897 | −3.9594 | −2.3572 | −1.1504 | −0.2095 | +.5422 | 1.1575 | 1.6702 | 2.1031 | 2.4749 | 2.8044 |
| $C_4H_{10}$(gas) = $C_4H_8$(gas) + $H_2$(ga) | −15.3715 | −15.2364 | −9.7090 | −6.3650 | −4.1017 | −2.4706 | −1.2443 | −.2990 | +.4758 | 1.1039 | 1.6302 | 2.0772 | 2.4551 | 2.7908 |
| $C_5H_{12}$(gas) = $C_5H_{10}$(gas) + $H_2$(gas) | −15.2070 | −15.0725 | −9.5615 | −6.2005 | −3.9550 | −2.3313 | −1.1050 | −.1492 | +.6177 | 1.2431 | 1.7653 | 2.2042 | 2.5838 | 2.9200 |
| n-Paraffin (gas) = 1-alkyne(gas) + 2$H_2$(gas): | | | | | | | | | | | | | | |
| $C_2H_6$(gas) = $C_2H_2$(gas) + 2$H_2$(gas) | −42.4103 | −42.0771 | −28.4239 | −20.1185 | −14.5303 | −10.4000 | −7.4498 | −5.0998 | −3.1634 | −1.6011 | −0.2992 | +0.8016 | 1.7437 | 2.5610 |
| $C_3H_8$(gas) = $C_3H_4$(gas) + 2$H_2$(gas) | −38.0619 | −37.8076 | −25.1853 | −17.4808 | −12.2940 | −8.5044 | −5.7546 | −3.5612 | −1.8058 | −0.3694 | +.8276 | 1.8385 | 2.7045 | 3.4820 |
| $C_4H_{10}$(gas) = $C_4H_6$(gas) + 2$H_2$(gas) | −38.3132 | −38.0028 | −25.2625 | −17.5354 | −12.3327 | −8.5030 | −5.7807 | −3.5875 | −1.8321 | −.3934 | +.8068 | 1.8220 | 2.6985 | 3.4415 |
| $C_5H_{12}$(gas) = $C_5H_8$(gas) + 2$H_2$(gas) | −38.2078 | −37.8975 | −25.1560 | −17.4156 | −12.2151 | −8.4778 | −5.6616 | −3.4678 | −1.7082 | −.2704 | +.9272 | 1.9376 | 2.8025 | 3.5608 |
| 1-Alkene(gas) = 1-alkyne(gas) + $H_2$(gas): | | | | | | | | | | | | | | |
| $C_2H_4$(gas) = $C_2H_2$(gas) + $H_2$(gas) | −24.7145 | −24.5277 | −16.8835 | −12.2171 | −9.0759 | −6.8128 | −5.1075 | −3.7706 | −2.7000 | −1.8240 | −1.0929 | −0.4750 | +0.0540 | 0.5118 |
| $C_3H_6$(gas) = $C_3H_4$(gas) + $H_2$(gas) | −22.9784 | −22.9154 | −15.6899 | −11.2911 | −8.3346 | −6.2072 | −4.6042 | −3.3517 | −2.3490 | −1.5269 | −0.8426 | −.2946 | +.2296 | .6576 |
| $C_4H_8$(gas) = $C_4H_6$(gas) + $H_2$(gas) | −22.9417 | −22.7694 | −15.5335 | −11.1704 | −8.2310 | −6.1224 | −4.5364 | −3.2985 | −2.3079 | −1.4973 | −.8234 | −.2532 | +.2204 | .6307 |
| $C_5H_{10}$(gas) = $C_5H_8$(gas) + $H_2$(gas) | −23.0036 | −22.8250 | −15.5975 | −11.2063 | −8.2901 | −6.1455 | −4.5566 | −3.3186 | −2.3259 | −1.5135 | −.8381 | −.2971 | +.2187 | .6408 |

The plots in figures 6, 7, 8, and 9 show, for molecules of the same number of carbon atoms, the range of temperature in which the normal paraffin, 1-alkene, and 1-alkyne hydrocarbons are relatively most stable (highest value of log $Kf$) in the presence of hydrogen, with each substance (including the hydrogen) in its thermodynamic standard state of unit fugacity of 1 atmosphere. These ranges of temperature are given in table 15 in degrees Kelvin and centigrade, and are important in the analysis of any process involving hydrogenation or dehydrogenation of these molecules.

TABLE 15.—*Ranges of temperature in which, for molecules of the same number of carbon atoms, the normal paraffin, 1-alkene, and 1-alkyne hydrocarbons, $C_2$ to $C_5$, are relatively most stable in the presence of hydrogen, with each substance in its thermodynamic standard state*

| Number of C atoms | n-Paraffin | | 1-Alkene | | 1-Alkyne | |
|---|---|---|---|---|---|---|
| | Range of temperature * | | | | | |
| | Below | | Between | | Above | |
| | °K | °C | °K | °C | °K | °C |
| $C_2$ | 1,065 | 792 | 1,065 to 1,390 | 792 to 1,117 | 1,390 | 1,117 |
| $C_3$ | 930 | 657 | 930 to 1,350 | 657 to 1,077 | 1,350 | 1,077 |
| $C_4$ | 935 | 662 | 935 to 1,350 | 662 to 1,077 | 1,350 | 1,077 |
| $C_5$ | 915 | 642 | 915 to 1,350 | 642 to 1,077 | 1,350 | 1,077 |

* Temperatures rounded to the nearest 5° $K$.

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WASHINGTON, June 1, 1945.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1683

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# REACTION OF PERIODIC ACID ON THE DIFRUCTOSE ANHYDRIDES

By Emma J. McDonald and Richard F. Jackson *

ABSTRACT

Diheterolevulosan, difructose anhydrides I, III, and II react, respectively, with 4, 2, 1, and 1 moles of periodic acid per mole of sugar. These results are in keeping with the known structures of the first three sugars. It is suggested that difructose anhydride II is a 1,2′-2,4′-difructofuranose.

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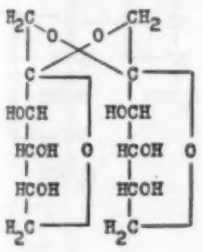
## I. INTRODUCTION

Four difructose anhydrides are known as crystalline compounds. Diheterolevulosan was first prepared by Pictet and Chavan [1] by the action of hydrochloric acid on levulose at 0° C. Difructose anhydrides I, II, and III were obtained by Jackson [2 3] and his coworkers from the residues after the removal of levulose when inulin was hydrolyzed with acid.

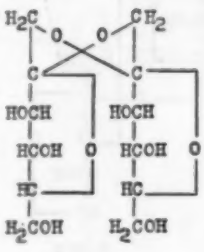
It has been shown that diheterolevulosan,[4] difructose anhydride I,[5] and difructose anhydride III [6] have the following structures:



I

Diheterolevulosan

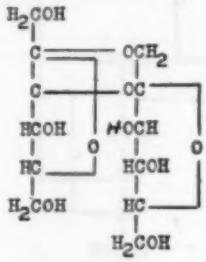
1,2′-2,1′-Difructopyranose anhydride



II

Difructose Anhydride I

1,2′-2,1′-Difructofuranose anhydride



III

Difructose Anhydride III

1,2′-2,3′-Difructofuranose anhydride

*Richard F. Jackson, deceased.

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[6] E. J. McDonald and R. F. Jackson, J. Research NBS **24**, 181 (1940) RP1277.

## II. DISCUSSION

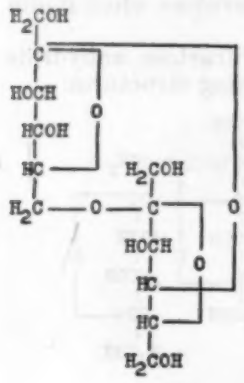
In the present investigation the reaction between periodic acid and the difructose anhydrides has been quantitatively studied. This acid has been used by many investigators [7 8 9] in structural studies because of its ability to react selectively with hydroxyls on adjacent carbon atoms.

In keeping with their known structures, diheterolevulosan reduces four moles of periodic acid per mole of anhydride, difructose anhydride I reacts with two moles, and difructose anhydride III with one mole of this acid.

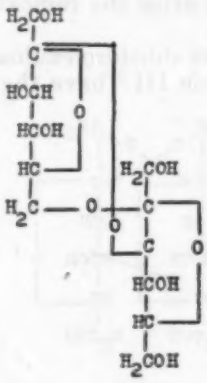
Haworth and Streight [10] have suggested that the stability of difructose anhydride I to acid might be attributed to the presence of the dioxane ring. The stability of diheterolevulosan and difructose anhydride III, both of which contain this dioxane grouping, is in keeping with this explanation.

In a previous investigation (see footnote 6) it has been shown that hexamethyl difructose anhydride II, upon hydrolysis, yields a product having a positive specific rotation of about 25 degrees. This appears to be composed of two trimethyl fructoses. The separation and purification of these partially methylated fructoses are being further studied.

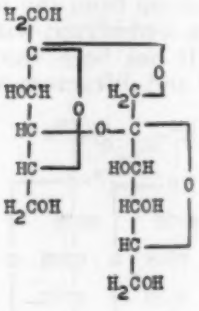
It is now shown that difructose anhydride II reacts with one mole of periodic acid. If we assume that, like the other two prepared from inulin, it is composed of fructofuranose units, there are 10 possible structures for this difructose anhydride. Only four of these would be expected to react with one mole of periodic acid. One of the four has been identified as difructose anhydride III. The remaining three are represented by formulas IV, V, and VI.



IV



V



VI

If formula IV represented difructose anhydride II, hydrolysis of the hexamethyl derivative would yield 1,3,6-trimethylfructose and 1,3,4-trimethylfructose. The latter is known as a crystalline product having a specific rotation of −51.4 in water. 1,3,6-Trimethylfructose is unknown, but it seems at least improbable that this derivative

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would have a rotation of +100 degrees. Thus, it seems unlikely that IV is the structure of difructose anhydride II.

An anhydride whose structure is represented by V would produce a mixture of 1,4,6- and 1,3,4-trimethylfructose upon hydrolysis of its hexamethyl derivative. Hydrolysis of hexamethyl difructose anhydride III is known to form 1,4,6-trimethylfructose along with 3,4,6-trimethylfructose. Since the latter is known to have a rotation of +30 degrees in water and the combined rotations are approximately this value, it follows that 1,4,6-trimethylfructose has a specific rotation in water solution of approximately +30 degrees. A mixture of 1,3,4-trimethylfructose and 1,4,6-trimethylfructose would rotate at approximately −10 degrees instead of +25 to +30 degrees. Thus, structure V is excluded.

The hydrolysis of the hexamethyl derivative of a sugar whose structure is represented by VI would yield 3,4,6-trimethylfructose and 1,3,6-trimethylfructose upon hydrolysis. Data now available are at least in accord with this structure.

## III. EXPERIMENTAL WORK

A solution containing 0.6367 g of diheterolevulosan in 50 ml of 0.2715-*M* $HIO_4$ was kept at 25° C for 15 hours. To 10 ml of this reaction mixture 1.5 g of $Na_2CO_3$ was added, followed by 31.008 ml of

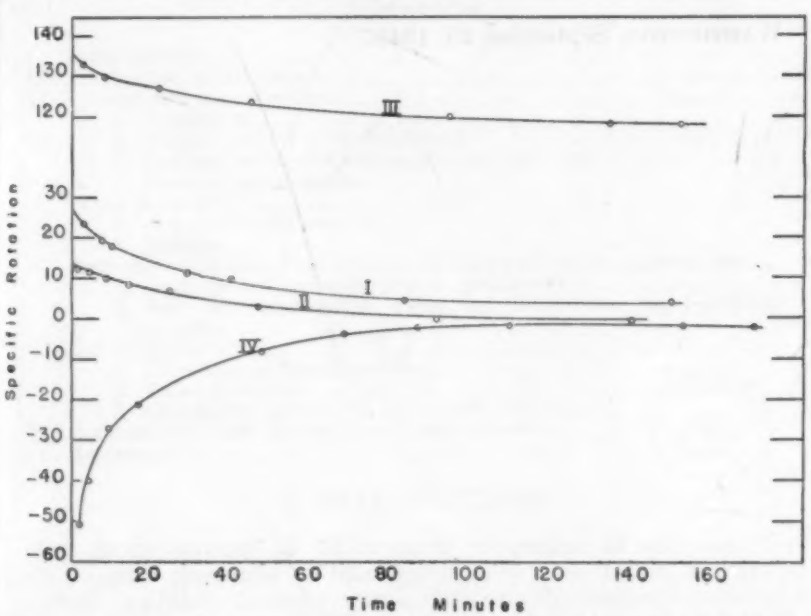


FIGURE 1.—*Rates of reaction of periodic acid and the difructose anhydrides.*

I. Difructose anhydride I. II. Difructose anhydride II. III. Difructose anhydride III. IV. Diheterolevulosan.

0.10095-*N* $As_2O_3$. One milliliter of 20-percent KI solution was then added, and after 15 minutes the unreacted $As_2O_3$ was determined by iodine titration. 8.456 ml of 0.1000-*N* iodine was required; thus,

22.629 ml of the $As_2O_3$ solution had reacted with the iodate present. This is equivalent to 4.188 ml of 0.2715-*M* periodic-acid solution and hence 5.812 ml, or 0.001578 mole, of acid was consumed by 0.000393 mole of sugar.

The difructofuranoses were treated by the same procedure. The number of moles of iodine reduced by one mole of the difructose anhydrides is given in table 1.

TABLE 1.—*Reacton of periodic acid and difructose anhydrides*

| | Mole of sugar | Time reacted | Mole of $HIO_4$ consumed | Mole of $HIO_4$ / Mole of sugar |
|---|---|---|---|---|
| | | *Hours* | | |
| Diheterolevulosan | 0.000393 | 3 | 0.00154 | 3.9 |
| | .000393 | 15 | .00158 | 4.0 |
| Difructose anhydride I | .000345 | 15 | .000660 | 1.9 |
| | .000345 | 18 | .000695 | 2.0 |
| Difructose anhydride II | .000337 | 4 | .000368 | 1.1 |
| | .000337 | 24 | .000370 | 1.1 |
| Difructose anhydride III | .000318 | 17 | .000324 | 1.0 |
| | .000318 | 44 | .000347 | 1.1 |

The progress of the reaction was followed polariscopically in each case, and the results are shown in figure 1.

WASHINGTON, September 25, 1945.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1684

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# THERMODYNAMIC PROPERTIES OF SOLID AND LIQUID ETHYLBENZENE FROM 0° TO 300° K

By Russell B. Scott and Ferdinand G. Brickwedde

**ABSTRACT**

The following properties of a sample of high purity ethylbenzene were measured: (1) Specific heat of solid and liquid from 15° to 300° K; (2) triple-point temperature (−95.005 ±0.010° C for pure ethylbenzene); (3) heat of fusion (86.47 int. j $g^{-1}$); (4) heat of vaporization at 294° K (400.15 int. j $g^{-1}$); and (5) vapor pressure from 273° to 296° K. With these experimental data, the enthalpy and entropy of the solid and of the liquid in the range 0° to 300° K were calculated.

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## I. INTRODUCTION

The measurements of the thermal properties of solid and liquid ethylbenzene described in this paper were undertaken as part of a program to obtain thermodynamic data on ethylbenzene covering the solid, liquid, and vapor phases and extending from 0° to 1,500° K. A calorimetric measurement of the specific heat of the vapor at 373.16° K was reported in an earlier paper [1] [1]; the calculated thermodynamic functions for the vapor from 300° to 1,500° K are reported in another paper [2].

[1] Figures in brackets indicate the literature references at the end of this paper.



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Ethylbenzene is important in the manufacture of synthetic rubber as it is converted into styrene by dehydrogenation, styrene being one of the two principal ingredients of GR-S (Government rubber-styrene type). Styrene is also used in making the plastic, polystyrene, a material much used for electrical insulation.

The properties measured and reported in this paper are as follows:

1. specific heat of solid and liquid ethylbenzene from 15° to 300° K,
2. triple-point temperature,
3. heat of fusion,
4. heat of vaporization at 294° K, and
5. vapor pressure in the temperature range 273° to 296° K.

By the use of the experimental data, calculations were made of the enthalpy and entropy of the solid and liquid from 0° to 300° K.

## II. PURIFICATION OF THE SAMPLE

The ethylbenzene used for the measurements was part of a sample distilled by M. R. Fenske of The Pennsylvania State College. The physical constants reported for the sample were 50 percent Cottrell boiling point, 136.25° C; index of refraction $n^{20}_d$=1.4958. The freezing point measured by Alfred Matuszak at the American Petroleum Institute Laboratories of Ohio State University was −95.02° C.

An additional purification by fractional crystallization was carried out at the National Bureau of Standards. Starting with a sample of about 600 ml, four fractionations were made and the unfrozen part of the sample poured off each time until about 150 ml remained. This material was then passed over finely divided silica gel in an 8-mm tube 50 cm long to remove water. It was then placed in a Pyrex bulb which communicated with the sample container of the calorimeter, and the air was removed by pumping until a high vacuum was obtained. The sample was then poured into the sample container of the calorimeter and sealed off while still under vacuum. The effectiveness of silica gel in removing water was verified by the fact that no cloudiness appeared in the sample when it was cooled to −80° C.

The amount of impurity was computed from measurements taken with the calorimeter, which gave the melting, or solid-liquid equilibrium, temperature of the sample as a function of the fraction melted. The temperature at which 50 percent of the sample was melted was found to be 0.002 degree centigrade lower than the temperature at which 99+ percent was melted. This indicates a *liquid soluble, solid insoluble* impurity of about 0.007 mole percent.

## III. CALORIMETRIC MEASUREMENTS

### 1. APPARATUS

Two different calorimeters were used for the measurements on solid and liquid ethylbenzene. They were similar in design to the calorimeter used by Southard and Brickwedde [3] but utilized a pure platinum resistance thermometer for the measurement of temperatures.

Calorimeter D, used for the measurement of the specific heats of solid and liquid ethylbenzene and for the measurement of the heat of fusion, had a capacity of 85 ml and was equipped with 18 vertical, radial vanes for the distribution of heat. The electric heater, which supplied the measured energy to the calorimeter, consisted of about

2 meters of No. 34 American Wire Gage fiber-glass insulated constantan wire wound on the outside of the platinum case of the resistance thermometer. The thermometer and heater were installed by immersing the assembly in molten solder (Sn-Pb eutectic) in the reentry well of the sample container. An aluminum cap was fastened over the bottom end of the sample container to trap radiation from the exposed ends of the constantan heater and from the thermometer. The heater and thermometer leads made one turn (cemented with Glyptal lacquer) around the sample container before crossing to the radiation shield.

Calorimeter C, used for the measurement of heat of vaporization, was the same calorimeter that had been used for measurements on 1,3-butadiene [4] and cis-2-butene [5]. It was provided with a tube for withdrawing vapor from the sample container. An important difference in the design of the two calorimeters was the disposition of the heaters. In calorimeter C, the heater was in a fine copper tube about 3 meters long wound as a helix inside the sample container, the helix having a radius about two-thirds that of the sample container. One effect of thus distributing the heater was to make the surface temperature of the calorimeter much more uniform while heat was being added.

Both calorimeters utilized three-element thermels for controlling the thermal shields and for exploring the temperature of the surface of the sample container. During operation of the calorimeters the multiple junction couples are used to maintain the thermal shield at the average temperature of the surface of the sample container.

The platinum resistance thermometers used for the temperature measurements were of the type described by Southard and Milner [6]. The calibration of the thermometers has been described by Hoge and Brickwedde [7].

## 2. SPECIFIC HEAT OF SOLID AND LIQUID

The results of the specific heat measurements are given in column 2 of table 1, tabulated at 5-degree intervals. These are smoothed results obtained by methods described in an earlier paper [4]. Figure 1 shows the deviations of the observed data from the smoothed table. The points shown in figure 1 were obtained by subtracting from the observed specific heat the specific heat obtained by interpolation from table 1.

It will be noted that two sets of points, designated by runs 2 and 3, show a pronounced departure from the table at temperatures below the triple point, the specific heat being considerably lower than that obtained in the other runs. Another peculiarity observed during runs 2 and 3, following the heats which terminated at a temperature a few degrees below the triple point, was that the temperature rose for a long time after adiabatic conditions had been established. This behavior could be explained if it is assumed that a small fraction of the sample remained liquid when the rest was frozen and that this supercooled liquid froze slowly when the temperature again approached the triple point. As heat would be given up by the freezing material it would account for both the temperature rise and the low apparent specific heat. Support for this explanation lies in the fact that ethylbenzene supercools readily.

TABLE 1.—*Specific heat, entropy and enthalpy* [a] *of solid and liquid ethylbenzene at saturated pressure*

[25.3770 cal mole$^{-1}$=1 int. j g$^{-1}$. $T$°K=$t$°C+273.16°. Atomic weights: C=12.010, H=1.0080.]

| $T$ | $C_{sat.}$ | $S_{sat.}$ | $(H_{sat.}-E_0^*)$ | $T$ | $C_{sat.}$ | $S_{sat.}$ | $(H_{sat.}-E_0^*)$ |
|---|---|---|---|---|---|---|---|
| SOLID | | | | LIQUID | | | |
| °K | *Int. j* $g^{-1}°K^{-1}$ | *Int. j* $g^{-1}°K^{-1}$ | *Int. j* $g^{-1}$ | °K | *Int. j* $g^{-1}°K^{-1}$ | *Int. j* $g^{-1}°K^{-1}$ | *Int. j* $g^{-1}$ |
| 0 | 0 | 0 | 0 | 178.155 | 1.4813 | 1.5898 | 187.67 |
| 5 | [b]0.00225 | 0.0007 | 0.0028 | 180 | 1.483 | 1.6050 | 190.40 |
| 10 | [b].01790 | .0060 | .0450 | 185 | 1.488 | 1.6457 | 197.83 |
| 15 | .0553 | .0196 | .219 | | | | |
| 20 | .1060 | .0423 | .621 | 190 | 1.494 | 1.6855 | 205.28 |
| | | | | 195 | 1.501 | 1.7244 | 212.77 |
| 25 | .1610 | .0718 | 1.286 | 200 | 1.508 | 1.7624 | 220.29 |
| 30 | .2184 | .1068 | 2.237 | 205 | 1.516 | 1.7998 | 227.85 |
| 35 | .2711 | .1440 | 3.463 | 210 | 1.524 | 1.8364 | 235.45 |
| 40 | .3177 | .1833 | 4.936 | | | | |
| 45 | .3601 | .2232 | 6.633 | 215 | 1.534 | 1.8724 | 243.10 |
| | | | | 220 | 1.543 | 1.9077 | 250.79 |
| 50 | .3991 | .2632 | 8.532 | 225 | 1.554 | 1.9425 | 258.53 |
| 55 | .4342 | .3029 | 10.617 | 230 | 1.565 | 1.9768 | 266.33 |
| 60 | .4662 | .3420 | 12.869 | 235 | 1.576 | 2.0106 | 274.18 |
| 65 | .4961 | .3806 | 15.276 | | | | |
| 70 | .5239 | .4184 | 17.826 | 240 | 1.588 | 2.0439 | 282.09 |
| | | | | 245 | 1.600 | 2.0767 | 290.06 |
| 75 | .5501 | .4554 | 20.512 | 250 | 1.612 | 2.1092 | 298.09 |
| 80 | .5760 | .4917 | 23.327 | 255 | 1.625 | 2.1412 | 306.19 |
| 85 | .6017 | .5274 | 26.272 | 260 | 1.639 | 2.1729 | 314.35 |
| 90 | .6249 | .5625 | 29.339 | | | | |
| 95 | .6463 | .5969 | 32.518 | 265 | 1.652 | 2.2043 | 322.57 |
| | | | | 270 | 1.666 | 2.2353 | 330.87 |
| 100 | .6678 | .6305 | 35.803 | 275 | 1.681 | 2.2660 | 339.23 |
| 105 | .6896 | .6637 | 39.196 | 280 | 1.696 | 2.2964 | 347.68 |
| 110 | .7110 | .6962 | 42.698 | 285 | 1.711 | 2.3266 | 356.19 |
| 115 | .7326 | .7283 | 46.306 | | | | |
| 120 | .7542 | .7599 | 50.024 | 290 | 1.726 | 2.3564 | 364.79 |
| | | | | 295 | 1.742 | 2.3861 | 373.46 |
| 125 | .7756 | .7912 | 53.848 | *298.16* | *1.753* | *2.4047* | *378.98* |
| 130 | .7971 | .8220 | 57.780 | | | | |
| 135 | .8186 | .8525 | 61.819 | 300 | 1.759 | 2.4155 | 382.21 |
| 140 | .8401 | .8827 | 65.966 | | | | |
| 145 | .8618 | .9125 | 70.220 | | | | |
| | | | | | | | |
| 150 | .8836 | .9421 | 74.584 | | | | |
| 155 | .9056 | .9714 | 79.057 | | | | |
| 160 | .9274 | 1.0005 | 83.639 | | | | |
| 165 | .9490 | 1.0294 | 88.330 | | | | |
| 170 | .9704 | 1.0580 | 93.129 | | | | |
| | | | | | | | |
| 175 | .9914 | 1.0865 | 98.034 | | | | |
| 178.155 | 1.0032 | 1.1043 | 101.18 | | | | |

[a] The enthalpy is referred to $H_0^*-E_0^*$, the internal energy of solid ethylbenzene at 0°K.

[b] Extrapolated by using the Debye function, $0.39983D(120/T)$.

It was thought that the anomolous behavior might be avoided if the sample were cooled slowly, during and after freezing, so this procedure was followed in subsequent runs. The data given in the legend of figure 1 show the thermal treatment of the sample preceding each run. By "fast" cooling is meant the removal of heat at a rate that caused the temperature to fall about 2 degrees per minute after the sample was completely frozen. "Slow" cooling was less than one-tenth this rate.

In preparing the smoothed table of specific heats, the results obtained in runs 2 and 3 below the triple point were not used. The results obtained in run 6 with calorimeter C were given less weight than the other observations because the sample container of calorimeter C was not full, hence the tare heat capacity was a greater part of the gross heat capacity than was the case with calorimeter D. The principal object of the measurements with calorimeter C was to provide an independent check on the accuracy of the measurements.

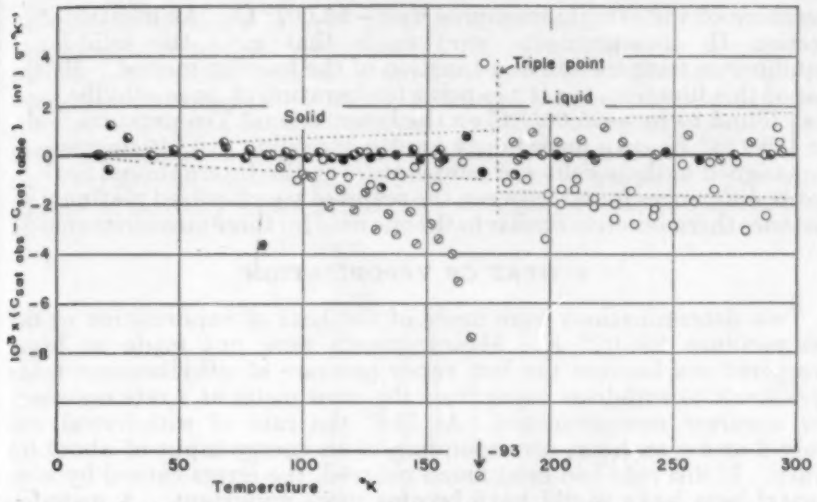


FIGURE 1.—*Deviations of observed specific heats from values obtained by interpolation from table.*

The triple-point temperature is indicated by the vertical dotted line. The dotted curves represent a deviation of ±1 part in 1,000. Symbols and information concerning the thermal treatment of the sample are given in the table below.

| Run | Symbol | Calorimeter | Rate at which sample was cooled after freezing started |
|---|---|---|---|
| 1 | ● | D | Fast |
| 2 | ⊘ | D | Do. |
| 3 | ⊘ | D | Do. |
| 4 | ◐ | D | Slow |
| 5 | ◑ | D | Do. |
| 6 | ○ | C | Do. |

The ratios of the heat capacity of the empty sample containers to that of the container plus sample were as follows:

| Temperature (°K) | Ratio | |
|---|---|---|
| | Calorimeter D | Calorimeter C |
| 15 | 0.13 | ---- |
| 90 | .41 | 0.55 |
| 175 | .39 | .52 |
| 290 | .29 | .42 |

### 3. HEAT OF FUSION AND TRIPLE-POINT TEMPERATURE

Four determinations of the heat of fusion were made. The methods of measurement and computation of data are described in an earlier paper [4]. The values obtained were 86.46, 86.45, 86.48 and 86.49 int. j $g^{-1}$, giving a mean value of 86.47 int. j $g^{-1}$. The triple-point tem-

perature of the sample measured was −95.007° C. As mentioned in section II, measurements were made that gave the solid-liquid equilibrium temperature as a function of the fraction melted. By the use of this function, the triple-point temperature of pure ethylbenzene was found to be −95.005° C on the International Temperature Scale, or 178.155° K. An uncertainty hardly exceeding ±0.010 degree is to be assigned to these values of temperature on the International Scale to cover differences found between the scales of standardized platinum resistance thermometers similar to the one used for these measurements [8].

### 4. HEAT OF VAPORIZATION

Two determinations were made of the heat of vaporization at the temperature 294.01° K. Measurements were not made at lower temperatures because the low vapor pressure of ethylbenzene made it difficult to withdraw vapor from the calorimeter at a rate necessary for accurate measurements. At 294° the rate of withdrawal was only 4 or 5 g an hour, corresponding to an energy input of about 0.5 watt. If this rate had been much reduced, the errors caused by accidental heat leaks would have become more important. A measurement of the heat of vaporization could not be made above room temperature because ethylbenzene vapor would have condensed in the part of the withdrawal tube at room temperature.

The two measurements of the heat of vaporization gave the values 399.81 and 400.49 int. j $g^{-1}$. The difference, 0.17 percent, is larger than the deviations usually obtained, but as the measurements were made under conditions of low vapor pressure the agreement is considered satisfactory.

## IV. VAPOR PRESSURE

### 1. APPARATUS AND METHOD

Figure 2 is a diagram of the apparatus used in measuring the vapor pressure of ethylbenzene. The sample, *S*, about 0.3 $cm^3$ of ethylbenzene, was contained in one of a pair of holes symmetrically placed in the copper cylinder, *C*. The other hole contains a platinum resistance thermometer, *Th*. The copper cylinder is suspended by two thin-walled monel tubes inside the hollow brass cylinder, *B*. In the present experiment there was air in the space between the cylinders, although, if desired, the space can be evacuated through the tube *Tu*. The desired temperature of the copper cylinder is maintained by a heating coil wound on the copper cylinder and a cold bath in the Dewar flask, *D*. The temperature of this bath was kept only 2 or 3 degrees below the temperature of the copper cylinder, so that only a small amount of electric energy was required to maintain the cylinder at a desired temperature. Radiation of heat from the inner or copper cylinder was reduced by covering it with aluminum foil. The temperature was kept constant to within 0.01 degree by manually controlling the current supplied to the heater, the necessary changes being indicated by the resistance theremometer.

Pressure measurements were made by means of the mercury manometer, *M*. The short cylinder at the top of the right-hand arm of the manometer has a diameter of about 25 mm and is provided with a glass point with which the mercury makes contact. Contact between the

mercury and the point is determined by observing the reflection, from the surface of the mercury, of a grating placed behind the tube, according to a method described by Stillman [9]. The mercury is brought into contact with the point by means of the injector, *I*, which consists of a stainless-steel piston 10 mm in diameter which displaces mercury in a stainless-steel cylinder of slightly larger diameter. The screw that forces the piston into the cylinder has a pitch of 1 mm, so that very fine adjustment of the mercury level is possible. The total amount of mercury in the manometer and injector can be adjusted by

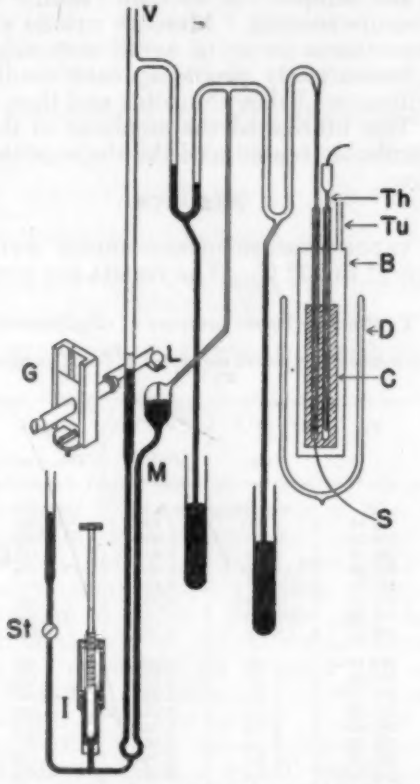


FIGURE 2.—*Apparatus for measuring the vapor pressure of ethylbenzene*

*V*, Vacuum line; *G*, comparator; *St*, stopcock; *I*, mercury injector; *M*, manometer; *Th*, platinum resistance thermometer; *Tu*, tube; *B*, brass cylinder; *D*, Dewar flask; *C*, copper cylinder; *S*, sample of ethylbenzene.

admitting or withdrawing mercury through the stopcock, *St*. The tubing of small diameter (5 mm) connecting the two sides of the manometer was covered with insulation to avoid temperature differences and resulting errors arising from unequal density of mercury in the two sides.

The left, or vacuum, arm of the manometer is 10 mm in diameter, and the mercury meniscus is lubricated with normal butyl phthalate [10] to minimize errors due to capillarity. The position of the mercury meniscus and the depth of the butyl phthalate are determined by the small comparator, *G*, which is mounted so that the microscope traverses a vertical path. An automobile headlight bulb, *L*, mounted

on a bracket attached to the comparator microscope so that the filament is on the axis of the microscope is a source of illumination that always maintains the same position relative to the mercury surface when a measurement is made. A green filter placed in the light path added to the comfort of reading and probably increased the sharpness of the image.

Measurements of vapor pressure were made by determining the positions of the mercury and butyl phthalate surfaces, first with both arms of the manometer evacuated, and then with the right arm communicating with the sample. A vacuum reading was taken before and after each pressure reading. Mercury cutoffs were used to make the necessary connections so as to avoid stopcock grease. It was found necessary, immediately preceding each reading, to lower the mercury a few millimeters below the point and then raise it until contact was made. This lubricated the meniscus in the left arm of the manometer, and probably reproduced the shape of the meniscus in the right arm each time.

## 2. RESULTS

Two series of vapor-pressure measurements were taken over the temperature range 0° to 23° C. The results are given in table 2.

TABLE 2.—*Vapor pressure of ethylbenzene*

Pressure in millimeters of mercury at standard conditions: 0° C and $g$=980.665 cm sec$^{-2}$. [$T$°K=$t$°C+273.16°.]

| $T$ | $P$ Obs. | $P$ Calc.[a] | $\Delta P$ Obs.−calc. |
|---|---|---|---|
| °K | mm Hg | mm Hg | mm Hg |
| 273.16 | 1.920 | 1.926 | −0.006 |
| 279.53 | 3.015 | 3.003 | .012 |
| 282.49 | 3.670 | 3.658 | .012 |
| 287.39 | 5.005 | 5.009 | −.004 |
| 290.36 | 6.017 | 6.024 | −.007 |
| 292.35 | 6.786 | 6.793 | −.007 |
| 294.61 | 7.772 | 7.768 | .004 |
| 296.61 | 8.739 | 8.734 | .005 |
| 273.16 | 1.931 | 1.926 | .005 |
| 275.73 | 2.310 | 2.311 | −.001 |
| 277.70 | 2.640 | 2.649 | −.009 |
| 279.66 | 3.024 | 3.031 | −.007 |
| 281.63 | 3.460 | 3.465 | .004 |
| 283.64 | 3.944 | 3.945 | −.001 |
| 289.58 | 5.754 | 5.745 | .009 |
| 292.14 | 6.703 | 6.711 | −.008 |

[a] $\log_{10} P_{(\text{mm Hg})} = 13.7540 - 3002.96/T - 0.0090634T$.

It was found that the observations were well represented by the equation

$$\log_{10} P_{(\text{mm Hg})} = 13.7540 - \frac{3002.96}{T} - 0.0090634T, \qquad (1)$$

where $P$ is the vapor pressure in millimeters of Hg reduced to standard conditions (0° C and $g$=980.665 cm sec$^{-2}$), and $T$ is the Kelvin temperature ($T$° K=273.16°+$t$° C). Column 3 of table 2 gives the values of the vapor pressure calculated from this equation and column 4 gives the difference between the observed and calculated pressures. The average deviation of the observations from the equation is 0.006 mm Hg.

## V. PROPERTIES DERIVABLE FROM THE CALORIMETRIC AND VAPOR-PRESSURE DATA

### 1. ENTROPY AND ENTHALPY OF SOLID AND LIQUID

In table 1, column 3, values of the entropy, $S_{sat.}$, of solid and liquid ethylbenzene at saturation pressure are given at 5-degree intervals. These were obtained by evaluating $\int_0^T (C_{sat.}/T)dT$, using tabular integration and Simpson's rule and adding at the triple point the entropy of fusion, $L_f/T_f$. Column 4 of table 1 gives values of the enthalpy $(H_{sat.}-E_0^\circ)$ at saturation pressure, referred to the internal energy of solid ethylbenzene at 0° K. The values of the enthalpy were obtained by evaluating $\int_0^T C_{sat.}dT$ and adding at the triple point the enthalpy of fusion, $L_f$. Strictly, the value of $(H_{sat.}-E_0^\circ)$ should include a term $\int_0^T v(dp/dT)_{sat.}dT$, but for the temperatures of the present investigation this term was negligible.

### 2. HEAT OF VAPORIZATION CALCULATED FROM THE VAPOR-PRESSURE EQUATION

The vapor-pressure equation, 1, was used with the Clausius-Clapeyron relation

$$L_v=T(V-v)\frac{dp}{dT} \tag{2}$$

to calculate the heat of vaporization of 294.01° K and thus provide a check on the accuracy of the measurements. In equation 2, $L_v$ is the heat of vaporization, $V$ is the specific volume of the saturated vapor, $v$ is the specific volume of the liquid, and $dp/dT$ is the derivative of the vapor-pressure–temperature relation. The specific volume of the saturated vapor at 294.01° K was computed by using the Berthelot equation of state with the critical constants $T_c=619.6$° K and $p_c=38.1$ atm, as determined by Altschul [11], and by using the vapor pressure 7.507 mm Hg calculated from equation 1. The value obtained was 22984 ml $g^{-1}$. The density of liquid ethylbenzene at 20° C is 0.868 g $ml^{-1}$ [12], which corresponds to a specific volume, $v$, of 1.15 ml $g^{-1}$. From equation 1, $dp/dT$ was found to be 0.44384 mm Hg °$K^{-1}$ at 294.01 °K. Substituting these values into equation 2, $L_v$ is found to be $2.9991\times10^6$ mm Hg ml $g^{-1}$, which, upon conversion, becomes 399.78 int. j $g^{-1}$. This is in good agreement with the directly measured heats of vaporization, being only 0.09 percent lower than the mean of the two calorimetric values.

## VI. ESTIMATE OF ERRORS

### 1. CALORIMETRIC MEASUREMENTS

Two tests were made to obtain evidence concerning the accuracy of the calorimetric measurements. In the first test the specific heat of air-free water, from 0° to 20° C, and its heat of vaporization at 20° C, were measured with calorimeter C. The results were in good agreement with the values reported by Osborne, Stimson, and Ginnings [13], the differences being of the order of 0.03 percent.

In the second test, calorimeter C was used to make some measurements between 90° and 295° K, on the same sample of ethylbenzene that had been investigated with calorimeter D. The average deviation between the values obtained with the two calorimeters was 0.10 percent.

The authors estimate that there is an even chance that the errors in the values of specific heat above 40° K given in table 1 and of the heat of vaporization reported in section III–5 do not exceed 0.1 percent. Below 40° K the errors in the specific heat measurements are larger, perhaps reaching 1 percent at 20° K. The value given for the heat of fusion, section III–4, may be somewhat more accurate than 0.1 percent because errors in measurement of temperature differences are less important.

### 2. VAPOR PRESSURE

An examination of the vapor-pressure data shows that about half of the observations deviate from the mean by more than 0.006 mm Hg. If systematic errors are negligible, this would indicate that the probable error of a single observation is 0.006 mm Hg. However, as errors caused by impurities or by prismatic effects in the manometer tube may well be systematic, too much confidence should not be attached to the figure indicated by the scattering of the observations.

### 3. CALCULATED VALUES OF ENTROPY AND ENTHALPY

As the calculated values of the entropy and enthalpy of the solid and liquid at saturation conditions involve only the errors of the calorimetric measurements, the probable error assigned to the reported values is 0.1 percent at the higher temperatures. Below 100° K errors in the entropy and enthalpy of the solid are probably larger because of the contributions of the less accurate specific-heat values below 40° K.

## VII. COMPARISONS WITH THE RESULTS OF OTHER OBSERVERS

In figure 3 the results of measurements by other observers of the specific heat of ethylbenzene are compared with the values obtained in this investigation. The ordinates of the graph are reported values of specific heat minus values obtained from table 1. The dotted curve represents a difference of 1 percent. The values reported by Guthrie, Spitzer, and Huffman [14] appeared while this paper was being prepared for publication. The agreement is good. Except in the region just below the triple point and at temperatures below 60° K, the differences seldom exceed 0.15 percent. The values given by Huffman, Parks, and Daniels [15] are, on the average, about 1 percent lower than those given in table 1. The values given by Blacet, Leighton, and Bartlett [16] are in fair agreement with the present values in the neighborhood of 300° K but are much lower at lower temperatures.

The heat of fusion as measured by Guthrie, Spitzer, and Huffman [14] was 86.31 int. j $g^{-1}$. Huffman, Parks, and Daniels [15] reported 86.32 int. j $g^{-1}$. These values are somewhat lower than the value 86.47 obtained in the present investigation. It is possible that the differences are the results of impurities in the samples. The purer

sample used in the present measurements permitted a more accurate determination of the specific heat of the solid in the region just below the triple point because there was less premelting. This results in an improved value of the heat of fusion because the actual measurement consists of heating the sample from a temperature below the triple point to a temperature above the triple point, and the heat required to raise the temperatures of the solid and liquid must be subtracted from the total energy supplied.

Osborne and Ginnings [17] measured the heat of vaporization of ethylbenzene at 25° C. They obtained the value 397.89 int. j $g^{-1}$. The mean value obtained in the present investigation was 400.15 int. j $g^{-1}$ at 294° K. In order to compare these values, the latter was

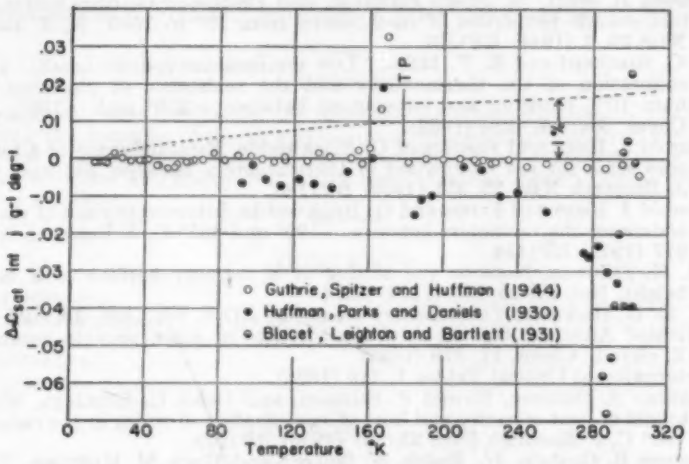


FIGURE 3.—*Comparison of the values of specific heat given in table 1 with the results of other observers.*

Ordinates represent the differences (observed values minus the values obtained from table 1). The distance between the dotted curve and the axis of zero ordinate represents a difference of 1 percent. The triple-point temperature is indicated by the vertical line labeled *TP*.

adjusted to correspond to the temperature 25° C (298.16° K) by means of the relation

$$dL/dT = C_p^\circ - C_{sat.\ liq.} - d/dT(H^\circ - H_{sat.\ vap.}). \quad (3)$$

The heat of vaporization at 298.16° K was found to be 397.92 int. j $g^{-1}$. This is in excellent agreement with the value of Osborne and Ginnings.

The vapor pressure of ethylbenzene was measured by Guttman, Westrum, and Pitzer [18] at temperatures between 0° and 60° C. They represented the results by the equation

$$\log_{10} P_{mm\ Hg} = -2959.08T^{-1} - 5.8 \log_{10} T + 25.25883. \quad (4)$$

This equation yields vapor pressures about 0.04 mm Hg higher than those obtained from equation 1 in the temperature range 273° to 297° K.

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The authors are indebted to M. R. Fenske, of The Pennsylvania State College, for the preparation of a pure sample of ethylbenzene for these measurements.

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# ASSEMBLY AND CALIBRATION OF A DENSITY BALANCE FOR LIQUID HYDROCARBONS[1]

By Alphonse F. Forziati,[2] Beveridge J. Mair, and Frederick D. Rossini

ABSTRACT

The assembly and calibration are described of a density balance for rapidly measuring the densities of liquid hydrocarbons on samples as small as 9 milliliters in volume. The reproducibility of the measurements is ±0.00002 to ±0.00003 gram per milliliter and the over-all uncertainty is estimated to be about ±0.00005 gram per milliliter.

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## I. INTRODUCTION

In connection with the work of this laboratory on the analysis, purification, and properties of hydrocarbons, it has been necessary to make measurements of the density of purified liquid hydrocarbons, and of mixtures of hydrocarbons, on samples as small as 9 ml in volume, rapidly and with a precision of several parts per 100,000. This report describes the assembly and calibration of a density balance for such measurements.

## II. APPARATUS

The assembly of the density balance is shown in figure 1, with the detailed parts described in the legends.

A diagram of the controls for the density balance is shown in figure 2, with details given in the legend.

The scale on this particular balance ranges[3] from 0.65 to 0.95 g/ml, with the smallest division on the chainomatic scale corresponding to 0.0001 g/ml and readings with the vernier being made to 0.00001 g/ml.

For containing the samples to be measured, test tubes having an inside diameter of 14 mm and an inside depth of 138 mm were se-

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the "Analysis, purification, and properties of hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

[3] Other ranges of scale readings may be obtained as required.

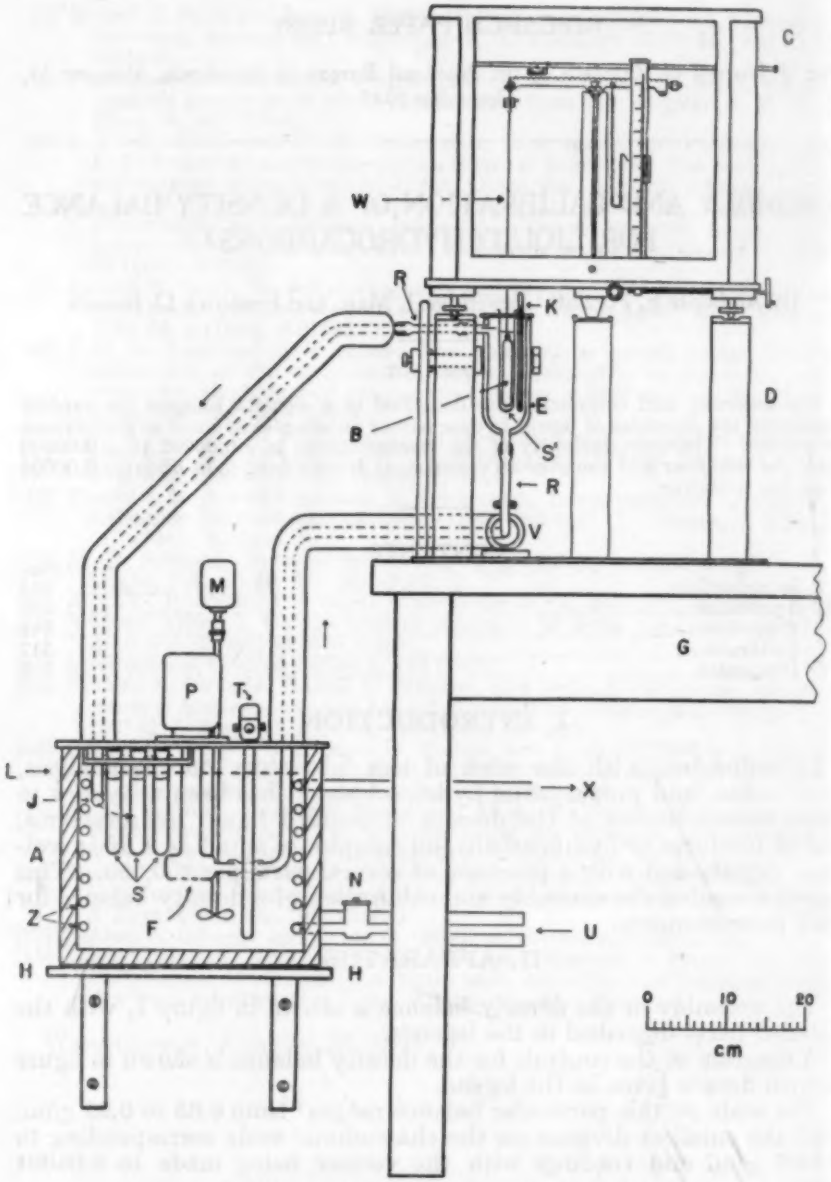


FIGURE 1.—*Assembly of density balance.*

*A*, Constant-temperature water reservoir; *B*, bob or plummet (volume 5 ml); *C*, chainomatic balance (see text); *D*, metal supporting stand; *E*, vacuum-jacketed glass water bath; *F*, water inlet to pump; *G*, table; *H*, shelf (fastened to wall); *J*, water return from *E*; *K*, special mercury-in-glass thermometer (graduated from 19.90 to 20.10, or from 24.90 to 25.10, or from 29.90 to 30.10, with a sensitivity on the scale of 1 mm equal to 0.05° C); *L*, level of water; *M*, motor for stirrer; *N*, solenoid valve; *P*, water pump; *R*, connection of rubber tubing; *S*, *S'*, test tubes for containing samples under observation; *T*, mercury-type thermoregulator; *U*, inlet for cooling water; *V*, valve for controlling flow of water through *E*; *W*, platinum wire, 0.003 inch in diameter; *X*, outlet for cooling water; *Z*, coil for cooling water.

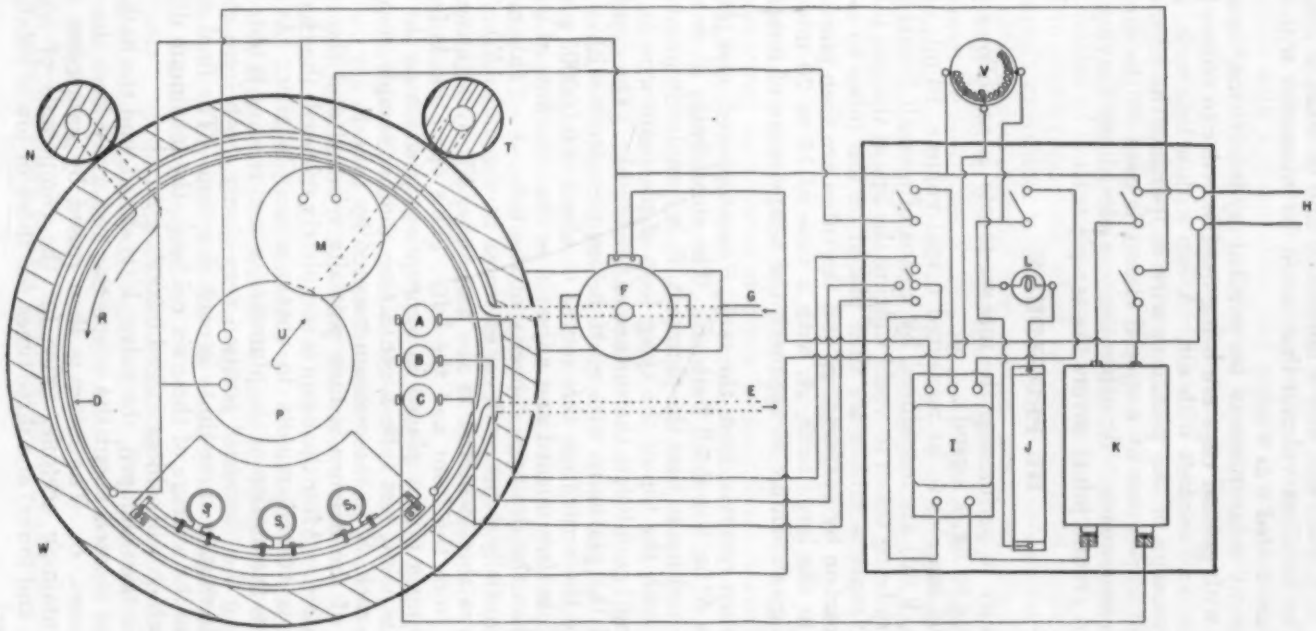


FIGURE 2.—*Diagram of controls of the density balance.*

*A, B, C,* Mercury-type thermoregulators, set to control at 20°, 25°, and 30° C, respectively, with a maximum amplitude in the control cycle of about 0.005° C; *D,* 100-watt heater in copper tube; *E,* discharge for water; *F,* solenoid valve (¾-in. iron-pipe connections); *G,* inlet for cooling water; *H,* electric-power line, 110-volt alternating current; *I,* relay (midget); *J,* 1,000-ohm resistance (10 watts); *K,* rectifying transformer, 110-volt alternating current to 6 volts, direct current; *L,* miniature lamp, 14 volts; *M,* stirrer motor; *N,* return for water; *P,* circulating water pump; *R,* water from *N*; $S_1$, $S_2$, $S_3$, test tubes containing samples for observation; *T,* thermally insulated pipe connecting large water reservoir and the vacuum-jacketed glass water bath; *U,* path of water to *T*; *V,* variable transformer, 115 volts alternating current, 100 watts; *W* constant-temperature water reservoir.

lected from standard Pyrex glass stock. On each tube was engraved a number (1, 2, 3, etc.) and also a horizontal line to mark a volume of 10 ml. The smallest volume that could be measured with the apparatus as assembled was 9 ml.

In more recent measurements on purified hydrocarbons,[4] special sample tubes with ground caps are being used in order to reduce loss by evaporation and contact with air. A cap with a hole in it, permitting free passage of the platinum wire supporting the plummet and being held in position by a special clamp, is used on the sample during the measurements. At other times, a closed cap (having the same standard ground joint) covers the sample tube.

## III. PROCEDURE

The procedure in performing the measurements is as follows (the letters referring to fig. 1 legend):

Three of the samples to be measured (usual volume, 10 ml; minimum volume, 9 ml) are introduced by means of a small funnel into test tubes, care being taken to avoid wetting the lips of the test tubes. Stoppers of Neoprene rubber are then placed on the tubes to avoid loss of hydrocarbon by evaporation, and the tubes are then placed in the rack, *S*, in the large bath, *A*, with a time of 15 to 20 minutes allowed for a given sample to approach the temperature of measurement.

Tube 1 is then removed from the rack, *S*, unstoppered, and placed in position at *S'* in the small bath, *E*. The small bath, *E*, is then elevated into position so that the plummet, *B*, is completely immersed in the liquid with the top of the tying loop of platinum wire on the plummet being 1 mm below the surface of the liquid. (The depth of immersion of the platinum wire must be kept constant within $\pm 1$ mm to reduce the error from this source to about $\pm 0.000005$ g/ml.) The valve, *V*, is then opened and adjusted so that the flow of water is just less than the drainage capacity of the tube, *J*. (This maintains a substantially constant level of water in the bath, *E*.) The plummet, *B*, is then centered in the test tube, *S'*, by sighting, at right angles, from the front and the left. (This operation is facilitated by having a mirror placed in appropriate position at the left side.) At this point, test tube 4, containing another sample, may be placed in the rack, *S*, in the position vacated by tube 1.

The beam of the balance is then partially released and the rider placed in position. After the beam is completely released, the chainomatic crank is turned rapidly to obtain a near balance. As the liquid dampens the motion of the plummet, a final reading is obtained by approaching the "balance" position very slowly, both from above and below, alternately three times in each direction. The final reading is taken as the average of these six readings, the maximum difference among which will seldom exceed 0.00002 g/ml.

The beam is then clamped, the valve, *V*, is closed, and the bath, *E*, is lowered and rotated about the supporting rod away from the suspended plummet, *B*. The latter is then rinsed by immersion in a test tube containing acetone, twice for the compounds of higher volatility ($C_7$ and lower) and three times for those of lower volatility ($C_8$ and higher).

[4] A. F. Forziati and F. D. Rossini, National Bureau of Standards. American Petroleum Institute Research Project 6. Unpublished data.

A period of 10 minutes is allowed for the plummet to become dry before immersing it in the next sample. During this interval, test tube 1 is removed from the small bath, *E*, the outside of the test tube is dried with a clean cloth, the sample is transferred to its original container, and the tube is cleaned by means of several rinsings with acetone and placed on the suction rack for drying.

At the beginning, middle, and end of each series of measurements, one of the standard reference liquids (2,2,4-trimethylpentane for paraffins, methylcyclohexane for naphthenes, and toluene for aromatics) is included among the samples measured in order to check the calibration of the balance (see following section).

The above procedure, which requires about 20 minutes per sample in steady operation, is that followed for the precise measurements on purified hydrocarbons. For routine analytical measurements (to $\pm 0.0001$ g/ml) on a series of fractions of distillate, considerable time is saved by eliminating some of the above steps; reducing the time of waiting for temperature equilibrium, eliminating some of the calibrations, etc. The abbreviated procedure requires about 10 minutes per sample in steady operation.

## IV. CALIBRATION

The balance was calibrated for measurements of density by making observations on a series of seven hydrocarbons (including the three NBS Standard Samples of hydrocarbons, which are certified with respect to values of density, namely, 2,2,4-trimethylpentane, No. 217; methylcyclohexane, No. 218; and toluene, No. 211 a), for which values of density were determined [5] under the supervision of E. L. Peffer in the Bureau's Capacity and Density Section, for air-saturated material, at 20°, 25°, and 30° C, with an estimated over-all uncertainty of $\pm 0.00002$ g/ml. In reducing the scale readings, corrections (from zero to 0.00003 g/ml) were made for slight inequalities in the spacing of the notches on the beam, which inequalities were determined by measurements with known masses hanging from the left arm of the beam as the rider on the beam was moved successively from one notch to another.

The results of the observations on the calibrating samples are given in figure 3, which gives on the scale of abscissas the scale reading and on the scale of ordinates the scale reading less the certified value of density, in $10^{-5}$ g/ml. For the measurements, the balance was adjusted so that, for 2,2,4-trimethylpentane (NBS Standard Sample 217) at 25° C, the scale reading was identical with the certified value for this temperature. Linear calibrating lines were drawn for each of the three temperatures, as shown, with the line for 25° C being made to go through zero at the density for the Standard Sample of 2,2,4-trimethylpentane.

Table 1 summarizes departure of the observed points in figure 3 from the appropriate calibrating line. It is seen that the maximum departure is $\pm 0.00003$ g/ml and that the average departures are $\pm 0.00002$ g/ml.

[5] The method is described in Tech. Pap. BS T77(1916) and Bul. BS **9**, 405 (1913) S197.

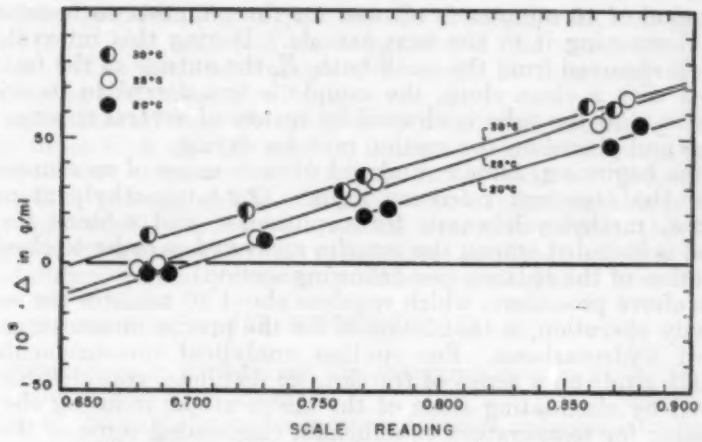


FIGURE 3.—*Calibrating data for the density balance.*

The scale of ordinate gives $10^5$ times the value of the difference, scale reading less the value of density certified for the given hydrocarbon, at the given temperature. The scale of abscissas gives the scale reading. The three sets of measurements apply to 20°, 25°, and 30° C, as indicated.

TABLE 1.—*Departures of the observations on the certified samples from the respective calibrating lines*

| Sample | Departure of the observed value from the value given by the calibrating line | | |
|---|---|---|---|
| | 20° C | 25° C | 30° C |
| | $10^{-5}$ g/ml | $10^{-5}$ g/ml | $10^{-5}$ g/ml |
| n-Heptane | 1½ | ½ | |
| 2,2,4-Trimethylpentane | −1 | 0 | 2½ |
| n-Decane | 1 | −3 | 1 |
| Methylcyclohexane | −1 | ½ | −2½ |
| Cyclohexane | −1 | 3 | 1 |
| Toluene | −2½ | −3 | 2½ |
| Benzene | 2½ | 3 | −2 |
| Average | ±1½ | ±2 | ±2 |

## V. DISCUSSION

As the density of liquid hydrocarbons changes about 0.00001 g/ml for a change in temperature of 0.01 deg C, and as the sensitivity of the balance is 0.00001 g/ml, changes in temperature of the sample under observation in excess of 0.01 deg will be reflected as changes in the scale readings at balance. For precise work, it is desirable to have a thermometric control that produces a maximum variation in the temperature of the sample of not more than 0.01 deg. In the apparatus assembled in this laboratory, the thermometric control produced temperatures having a maximum variation of about 0.005 deg. The absolute value of the temperature of the measurements made at the three controlled temperatures was determined at appropriate intervals by placing a platinum resistance thermometer (25 ohms) in place of the plummet and determining the resistance of the platinum thermometer with a Mueller bridge. The same observations yielded the magnitude of the variation of the temperature.

The effect, on this method of measuring density, of differences in surface tension of the samples under investigation, with resulting different forces on the thin platinum wire supporting the plummet, was calculated to be negligible. Because the surface tension of hydrocarbons varies in a more or less regular manner with density, the main effect of differences in surface tension in going from hydrocarbons of low density to those of high density becomes incorporated as part of the calibration correction. The net effect of surface tension then reduces to the effect of the difference in surface tension for hydrocarbons of the same or nearly the same density. Examination of the available data indicates that, in the range of density 0.60 to 0.90, hydrocarbons of the same or nearly the same density have values of surface tension that differ by not more than about one dyne/cm. This would correspond to a maximum error of 0.000005 gm/ml in density.

The effect, on the density, of absorption by the hydrocarbon of water vapor from the air was determined by measuring the difference between the density of a sample dried by filtration through silica gel and of this same sample subsequently saturated with water. The observed differences, density of sample saturated with water less the density of the dried sample, were 0.00001, −0.00001, and −0.00003 g/ml for 2,2,4-trimethylpentane, methylcyclohexane, and toluene, respectively. During the measurements on the material saturated with water, a globule of water was permitted to lie at the bottom of the tube containing the hydrocarbon. With normal precautions, it appears that errors from this source are well within the limits of uncertainty.

In order to ascertain whether the measurements as made are for hydrocarbon saturated with air, the difference was determined between the density of a freshly distilled sample and of this same sample subsequently saturated with air. The observed differences, density of freshly distilled sample less that of the air-saturated sample, were −0.00001, 0.00001, and 0.00001 g/ml for 2,2,4-trimethylpentane, methylcyclohexane, and toluene, respectively. It appears that measurements made by the present procedure may be ascribed, well within the limits of uncertainty, to hydrocarbon material saturated with air.

From the results of repeated observations on various samples, the reproducibility of the observations made with this density balance is estimated to be ±0.00002 to ±0.00003 g/ml. From the data given in table 1 and figure 3, the over-all uncertainty of the measurements of density of a given sample is estimated to be about ±0.00005 g/ml.

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The authors are indebted to E. L. Peffer, chief of the Bureau's Capacity and Density Section, for providing the absolute values of the densities of the reference and Standard Samples used in the calibrations reported in this paper.

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# ULTRAVIOLET SPECTRA AND DISSOCIATION CONSTANTS OF *p*-HYDROXYBENZOIC ACID, METHYL, ETHYL, *n*-BUTYL, AND BENZYL *p*-HYDROXYBENZOATE AND POTASSIUM *p*-PHENOLSULFONATE

By Elizabeth E. Sager, Marjorie R. Schooley, Alice S. Carr, and S. F. Acree

**ABSTRACT**

The apparent first and second dissociation constants of *p*-hydroxybenzoic acid, the constants for the phenol group of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate, and potassium *p*-phenolsulfonate have been determined from ultraviolet spectral data. The compounds have wide absorption bands located in the region of 200 to 400 mμ, and the differences between the transmittancy curves for their ionic and molecular forms are great enough to permit the measurement of several intermediate steps in the transformation at various pH values. The buffers used to control the dissociation were acetates, phosphates, and borates, all of low ionic strengths. Esterification of the carboxyl group of *p*-hydroxybenzoic acid apparently increases the dissociation of the phenol, and p$K^*$ decreases from 9.3 for the second dissociation of the acid to 8.3 for the esters. The thermodynamic dissociation constants are estimated.

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## I. INTRODUCTION

The dissociation constants of many organic compounds have been determined by electromotive-force and conductivity methods. The

constants of several indicators have also been calculated from spectrophotometric measurements, by the use of quantitative changes in color in the visible part of the spectrum, corresponding to known changes in hydrogen-ion concentration of the indicator solutions.

Colorless compounds transmit light completely in the visible region of the spectrum but have absorption bands in the ultraviolet, the positions of which have been reported by various investigators. Most of the published data were obtained by spectrographic methods, which involve density measurements of photographic plates. The experimental errors of such determinations are acknowledged to be large. In a recent spectrophotometric study of a buffer compound [1] [1] it was shown that measurements in the ultraviolet from 200 to 400 m$\mu$ can be obtained by means of a photoelectric spectrophotometer [2] with sufficient accuracy to calculate the dissociation constant. The behavior of *p*-phenolsulfonic acid, its primary potassium salt, and its secondary potassium-sodium salt was illustrated by the spectral data. The change in the absorption index with variation in the hydrogen-ion concentration was of the same order of magnitude as encountered with indicators in the visible portion of the spectrum. By employing other buffers, such as phosphates and borates, whose absorption bands are not in the same region of the spectrum, the degree of transformation was controlled and measured quantitatively.

In many cases the use of ultraviolet spectrophotometry in the study of electrolytic solutions possesses decided advantages. One may obtain the limiting curves for the ionic or the molecular form of a compound in acid, in alkali, or in buffers of known pH, and thus shed light upon the behavior of the molecule. A large number of organic and inorganic compounds have been investigated by this means, and transmittancy curves have been obtained for various concentrations in water, hydrochloric acid, sodium hydroxide, and in buffers.

The spectrophotometric method is the only known means of determining the dissociation constants of many difficultly soluble compounds whose saturated solutions have concentrations less than approximately $10^{-3}$ molar.[2] For the more soluble compounds, the electromotive-force and conductance methods may often be supplemented advantageously by the spectrophotometric study and a measurement of the concentrations of the ion and mole forms obtained.

The data presented in this paper illustrate the application of the method to calculations of the first and second dissociation constants of *p*-hydroxybenzoic acid and of the dissociation constant of the phenol group of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate, and potassium *p*-phenolsulfonate. The dissociation of the two groups of *p*-phenolsulfonic acid has also been recently studied by electromotive-force methods [3, 4]. The esters of *p*-hydroxybenzoic acid are representative of compounds difficulty soluble in water. Their dissociation constants have not been reported by any one of the three methods mentioned above. Several of the substituted benzoic acids have been studied and reported [5]. The value of the spectrophotometric method is well illustrated by the data for *p*-hydroxybenzoic acid, where the two steps in the dissociation can be differentiated by a study of the spectral transmittancies.

[1] Figures in brackets indicate literature references at the end of this paper.
[2] The symbol *M* will hereafter be used to designate "molar."

## II. MATERIALS

The compounds investigated were obtained from commercial firms, and were further purified in some cases when the melting points and spectrophotometric curves indicated the presence of impurities. Before use, the white crystalline compounds were dried to constant weight in a vacuum oven at about 3- to 5-mm pressure and at temperatures ranging from 30° to 60° C.

The *p*-hydroxybenzoic acid, after two recrystallizations from distilled water, had a melting point of 211° to 213° C. The methyl and ethyl *p*-hydroxybenzoate were used without further purification. Their melting points were 125° to 126° C and 115.5° to 116° C, respectively. The *n*-butyl and benzyl *p*-hydroxybenzoate were each recrystallized once from water, and their melting points were 70° and 112° C, respectively. The potassium *p*-phenolsulfonate was purified by several recrystallizations from water. Its purity was found to be 100.03 percent by bromometric assay, as described in an earlier publication [1]. The solubilities of the different compounds were not determined.

The phosphate buffers were prepared from disodium hydrogen phosphate and sodium dihydrogen phosphate of known purity [6]. The borate buffers [7] were prepared from recrystallized boric acid, recrystallized borax, and 0.1-*M* sodium hydroxide, prepared free from carbonate. The acetate buffers were prepared from reagent-grade acetic acid and sodium hydroxide. Solutions of hydrochloric acid were prepared by dilution of material of reagent grade.

## III. EQUIPMENT

### 1. SPECTROPHOTOMETRIC EQUIPMENT

All the spectrophotometric measurements were made over a spectral range of 200 to 400 mμ with a quartz photoelectric spectrophotometer [2]. The cell compartment was remodeled so that absorption cells previously constructed for indicator studies [8] could be used. The cells consisted of Pyrex tubing, 3.8 cm in diameter and 1-, 2-, and 5-cm in length. The ends were polished and fitted with removable quartz plates. Cells and end plates were held tightly together by metal holders. For the measurement of the transmittancies of solutions, two absorption cells of the same length were used. One contained the solvent alone and the other contained the compound under investigation, dissolved in the solvent. A special slide in the cell compartment of the spectrophotometer permitted movement of the cells into positions axial with the light beam.

Balance of the spectrophotometer was accomplished by adjusting the slit-width for the entrance and exit of the light beam, with the solvent cell in the beam. This setting corresponded to a transmission reading of 100 percent. The slit-width was small (less than 1 mm) for most wavelengths, and changes in slit-width caused no appreciable error in the values for the wide absorption bands characteristic of these solutions. When a balance of the needle was obtained for the solvent cell, the other cell was moved to the same position in the beam, and a measurement of the transmittancy of the unknown compound was made. Inasmuch as the absorptions of the four crystalline quartz end plates differed slightly at the lower wavelengths, the pair showing the least absorption was always used for the solvent cell.

All the equipment was used in a room maintained at 25° C. In order to eliminate a rise in temperature of the solutions because of the proximity of the light source, the cell compartment of the spectrophotometer was fitted with an inlet and an outlet tube, through which a slow stream of air was drawn from the constant-temperature room. The temperature of the solutions thus remained at 25° to 26° C. For some of the measurements, an especially designed water-jacketed hydrogen arc [3] was used. This source of light was sufficiently intense for use at wavelengths as low as 200 mμ.

### 2. ELECTROMETRIC EQUIPMENT

The pH measurements were made at 25° C with commercial glass-electrode assemblies. The pH meter was calibrated with a 0.05-*M* solution of potassium acid phthalate, the pH of which is 4.008 at 25° C [9]. Frequent checks were made with a phosphate buffer, pH 7.01, and a borax buffer, pH 9.18. These standard pH values were computed on the activity basis, and the measured pH is therefore assumed to represent the negative of the logarithm of the activity of hydrogen ion. Although most of the buffers used in this work had ionic strengths less than 0.05, a few experiments were made with additional phthalate buffers of 0.01-, 0.02-, and 0.10-*M* concentrations. The glass-electrode readings agreed with the calculated values [9] within the error of the instrument (0.01 pH unit). The readings are considered to be reasonably free from errors which might be attributed to liquid-junction potentials and are believed to be correct within ±0.02 pH unit.

## IV. EXPERIMENTAL PROCEDURE

### 1. PROVISIONAL TRANSMITTANCY MEASUREMENTS

The procedure found to be the most useful was to measure first the absorption of a $10^{-2}$-*M* aqueous solution of the compound with the 1-cm absorption cells. This measurement served to locate the "cutoff" position of the band nearest the visible region, in which the transmittancies varied from 0 to 100 percent within a wavelength range of about 10 to 20 mμ. For difficultly soluble compounds, it was necessary to use lower concentrations and longer absorption cells. When concentrations as low as $10^{-4}$ to $10^{-5}$ *M* were used, all bands were usually located by a series of dilutions in approximately tenfold steps.

The limiting spectral curves that represent the ionic and molecular forms of the compound were next determined by employing buffers that covered a wide pH range, or a 0.1-*M* solution of strong acid and a $10^{-2}$-*M* solution of strong alkali. When the absorption bands remained unchanged over a considerable range of pH (1 or more units), it was assumed that the spectral curves were those of the limiting forms. A few additional experiments at intermediate pH values resulted in a set of intersecting curves that gave a rough spectral pattern of the behavior of the compound. From the transmittancy values at a given wavelength, calculations of the amount of the molecular form transformed to the ionic form, or vice versa, were made, and these values were plotted as a function of pH. From these data, the pH steps and corresponding buffers to cover the range were

[3] Made by Austin G. Nester, Swarthmore, Pa.

selected. The solutions required to obtain the necessary spectrophotometric curves were then prepared.

### 2. SELECTION OF BUFFERS

The selection of buffers for spectrophotometric work in the ultraviolet presents a more complicated problem than does the choice of buffers suitable for the visible region. Not only must a wider pH range be covered, which usually requires more than one buffering system, but the choice is limited to buffers whose absorption bands do not lie in the same spectral region as the bands of the compounds under study. The "cutoff" positions of many buffer compounds of about 0.01-*M* concentration have already been determined in 1-cm absorption cells.[4]

In order to prevent distortion of the spectrophotometric curves by specific salt errors, it is desirable to keep the ionic strength of each buffer as low as possible, without sacrifice of buffering capacity. In earlier published work on the acid range of metacresolsulfonphthalein in the visible region [8], it was shown that the intermediate and complete transformation of this indicator could be accomplished simply by the use of solutions of hydrochloric acid of concentrations ranging from about $10^{-3}$ to 2 *M*. Provisional measurements of several other indicators in the visible and in the ultraviolet have now been obtained by use of phthalates, benzoates, citrates, phosphates, and phenolsulfonates, in addition to hydrochloric acid and sodium or potassium hydroxide. With buffers of ionic strength of about 0.01, transmittancy measurements may be made above 220 mμ with the acetates, above 230 mμ with the citrates, and above 280 to 300 mμ with the benzoates, phenolsulfonates, and phthalates. Hydrochloric acid in concentrations up to 2 *M* satisfactorily transmits wavelengths greater than 200 mμ. The phosphates and borates of low ionic strengths transmit at wavelengths longer than 205 mμ. Sodium and potassium hydroxide transmit above about 215 mμ. The lower limit depends upon the concentration of the hydroxyl ion. There was considerable evidence of adverse influence of phosphate buffers on the transmittancies of potassium phenolsulfonate in the ultraviolet and of metacresolsulfonphthalein in the visible. Other buffers such as the acetates or borates may also have some specific effect and should be studied. The poor isosbestic points in many of the series of curves for the transformation of indicators may be attributable to the use of buffers of high ionic strengths.

### 3. GENERAL PROCEDURE

The solutions were prepared at 25° C in a constant-temperature room by volumetric methods. For both the spectrophotometric and the pH measurements, 100 ml of each solution was sufficient. It was convenient to use 10 ml of stock solution of the compound under investigation with 90 ml of buffer. For the comparison solution, 10 ml of water and 90 ml of buffer were used.

Before a series of spectrophotometric measurements was started, the two pairs of end plates were carefully cleaned, the cells assembled and filled with water, and a calibration was made over the spectral range to be covered. This was accomplished by measuring the transmission of the solution cell against the transmission of the sol-

[4] Unpublished work of E. E. Sager, M. R. Schooley, A. S. Carr, and S. F. Acree. A preliminary report appeared in the March 1944 issue of the NBS Technical News Bulletin.

vent cell, which was set at 100 percent. Any differences may be attributed to differences in absorption of the pairs of end plates. As there were differences at the shorter wavelengths in the crystal quartz end plates used in these experiments, the end plates were marked and the same pair were always used for the same cell. The transmission of the solution cell was 95 percent of that of the solvent cell at 200 mμ. The transmissions approached equality at about 225 mμ, and the cells were considered to be clean if they "balanced" within 0.2 percent transmittancy at wavelengths longer than 225 to 230 mμ. To make the calibration, readings were taken at 1, 2, or 5 mμ from 200 to 225 mμ and at intervals of 10 mμ from 225 to 400 mμ. The same procedure was followed at the end of each series of measurements or at the end of the day, to assure that no film adhered to the end plates during the measurements. A calibration curve for the water was drawn, from which the corrections to be made to the transmittancy values of the solutions could readily be obtained. The absorption cells were reassembled daily.

For each spectral curve, one cell was filled with the desired concentration of the compound in the chosen solvent medium and the other was filled with the solvent. In all cases the solvent consisted of water, acid, alkali, or buffer solution. Before the transmittancy measurements were made progessively over the desired wavelength range, a few readings were made at selected wavelengths. Readings for the entire curve were then made, at intervals of 2 mμ. Near the maxima and minima of the bands, readings were usually made at intervals of 1 mμ. The selected wavelengths were checked in the reverse order. If agreement in these transmittancies was within the experimental error, it was assumed that no change had taken place in the solution during the time required for the readings. The reproducibility of the transmittancies at a given wavelength was usually $\pm 0.001$ from 230 to 400 mμ and $\pm 0.005$ from 200 to 230 mμ, where the precision in setting the dials of the spectrophotometer is least. About 20 to 30 minutes is required for an experienced operator to make measurements over the ultraviolet range alone.

## V. CALCULATIONS FROM THE SPECTROPHOTOMETRIC DATA

### 1. APPLICATION OF BEER'S LAW

A pure compound in solution has a characteristic spectral-absorption curve, and at any given wavelength the molar absorption index, $k$, is calculated by eq 1, derived from Beer's law:

$$k=\frac{-\log_{10} t}{dM}, \tag{1}$$

in which $t$ is the transmittancy of the solution, $d$ is the thickness of the absorbing layer in centimeters (cell length), and $M$ is the molar concentration of the compound. The value for $k$ at any selected wave length should be the same, unless impurities are present or some reaction, such as dissociation or hydrolysis, is taking place. In order to determine the validity of Beer's law, one may compare the values of $k$, measuring several different concentrations of the compound in a cell of the same depth or by use of the same concentration in cells of different lengths. For each compound reported in this paper, Beer's law was found valid. The experiments included either

two or more concentrations in the 1-cm absorption cells, or the same concentration in cells of 1-, 2-, and 5-cm lengths. The data for all of the compounds are too extensive for publication. However, to demonstrate their accuracy, the data for potassium *p*-phenolsulfonate are given. The transmittancies and the corresponding molar absorption indices are shown in table 1. The resulting ratios of the indices for three concentrations are given for several wavelengths.

TABLE 1.—*Beer's law applied to potassium p-phenolsulfonate in 0.1-M* HCl, *a borate buffer, and 0.001-M* NaOH

[Comparison of the molar absorption indices of three concentrations in 1-cm absorption cells]

| Wavelength | A, $2.999\times10^{-4}$ *M* | | B, $4.003\times10^{-4}$ *M* | | C, $5.000\times10^{-4}$ *M* | | Ratios | |
|---|---|---|---|---|---|---|---|---|
| | Transmittancy | $k_A$ | Transmittancy | $k_B$ | Transmittancy | $k_C$ | $k_B/k_A$ | $k_B/k_C$ |
| **IN 0.1-*M* HCl, pH 1.04** | | | | | | | | |
| mμ | | | | | | | | |
| 220 | 0.610 | 7158 | 0.516 | 7170 | 0.439 | 7151 | 1.003 | 1.004 |
| 222 | .554 | 8552 | .456 | 8520 | .374 | 8543 | 0.996 | 0.997 |
| 224 | .504 | 9922 | .402 | 9888 | .320 | 9898 | .997 | .999 |
| 226 | .461 | 11213 | .359 | 11115 | .278 | 11120 | .991 | 1.000 |
| 228 | .432 | 12154 | .329 | 12062 | .250 | 12042 | .992 | 1.002 |
| 229 | .423 | 12459 | .320 | 12363 | .242 | 12325 | .992 | 1.003 |
| 230 | .420 | 12562 | .318 | 12431 | .239 | 12433 | .990 | 1.000 |
| 231 | .421 | 12527 | .319 | 12397 | .240 | 12397 | .990 | 1.000 |
| 232 | .428 | 12289 | .326 | 12161 | .248 | 12112 | .990 | 1.004 |
| 234 | .458 | 11307 | .356 | 11206 | .275 | 11214 | .991 | 0.999 |
| 236 | .513 | 9665 | .412 | 9621 | .334 | 9526 | .995 | 1.010 |
| 238 | .592 | 7591 | .501 | 7499 | .422 | 7494 | .988 | 1.001 |
| 240 | .693 | 5310 | .619 | 5204 | .548 | 5225 | .980 | 0.996 |
| | | | | | | | avg 0.992 | avg 1.001 |
| **IN BORATE BUFFER, pH 8.98** | | | | | | | | |
| 244 | 0.630 | 6690 | 0.540 | 6686 | 0.463 | 6689 | 0.999 | 1.000 |
| 246 | .611 | 7134 | .520 | 7095 | .443 | 7073 | .995 | 1.003 |
| 248 | .586 | 7739 | .491 | 7718 | .413 | 7682 | .997 | 1.005 |
| 250 | .565 | 8267 | .465 | 8308 | .387 | 8246 | 1.005 | 1.007 |
| 251 | .558 | 8448 | .455 | 8544 | .376 | 8497 | 1.011 | 1.006 |
| 252 | .550 | 8657 | .449 | 8688 | .370 | 8637 | 1.004 | 1.006 |
| 253 | .548 | 8710 | .445 | 8785 | .364 | 8779 | 1.009 | 1.001 |
| 254 | .545 | 8789 | .444 | 8810 | .364 | 8779 | 1.002 | 1.004 |
| 255 | .550 | 8657 | .447 | 8736 | .368 | 8684 | 1.009 | 1.006 |
| 256 | .557 | 8474 | .453 | 8592 | .377 | 8474 | 1.014 | 1.014 |
| 258 | .582 | 7838 | .481 | 7941 | .406 | 7830 | 1.013 | 1.014 |
| 260 | .622 | 6876 | .524 | 7012 | .448 | 6975 | 1.020 | 1.005 |
| 262 | .672 | 5756 | .581 | 5892 | .512 | 5815 | 1.024 | 1.013 |
| | | | | | | | avg 1.008 | avg 1.006 |
| **IN 0.001-*M* NaOH, pH 11** | | | | | | | | |
| 244 | 0.435 | 12053 | 0.327 | 12128 | 0.250 | 12042 | 1.006 | 1.007 |
| 246 | .383 | 13897 | .278 | 13890 | .202 | 13894 | 0.999 | 1.000 |
| 248 | .341 | 15579 | .237 | 15620 | .168 | 15494 | 1.003 | 1.008 |
| 250 | .310 | 16959 | .209 | 16985 | .142 | 16955 | 1.001 | 1.002 |
| 251 | .299 | 17482 | .200 | 17462 | .134 | 17459 | 0.999 | 1.000 |
| 252 | .290 | 17925 | .193 | 17849 | .130 | 17722 | .996 | 1.007 |
| 253 | .287 | 18075 | .191 | 17962 | .126 | 17993 | .994 | 0.998 |
| 254 | .288 | 18025 | .190 | 18019 | .128 | 17857 | 1.000 | 1.009 |
| 255 | .290 | 17925 | .192 | 17905 | .130 | 17722 | 0.999 | 1.010 |
| 256 | .300 | 17434 | .198 | 17571 | .135 | 17394 | 1.008 | 1.010 |
| 258 | .330 | 16054 | .227 | 16088 | .160 | 15918 | 1.002 | 1.011 |
| 260 | .381 | 13973 | .273 | 14086 | .201 | 13937 | 1.008 | 1.010 |
| 262 | .450 | 11563 | .343 | 11610 | .263 | 11601 | 1.004 | 1.001 |
| | | | | | | | avg 1.001 | avg 1.006 |

In calculating numerical quantities from spectral data, one should remember that the experimental transmittancy values may easily be in error by 0.001 to 0.002. However, it is the error in the logarithm ($-\log t$) that is significant. When transmittancies below 0.1 and above 0.9 are used, additional errors are involved. The ratios given in table 1, therefore, include all experimental errors, such as dilution error or temperature effects, as well as instrumental errors in the spectrophotometric measurements.

## 2. CALCULATION OF THE "APPARENT" DISSOCIATION CONSTANTS

The molar absorption indices, $k$, are calculated from the transmittancies at any wavelength by eq 1. The indices $k_m$, $k_i$ and $k_a$ are those of the molecular form, the ionic form, and a mixture of the two, respectively. From the indices at a given wavelength, $\alpha$ is calculated by eq 2:

$$\alpha=(k_a-k_m)/(k_i-k_m). \tag{2}$$

$\alpha$ represents the amount of the electromeric forms of the acid or ester transformed to the electromeric forms of the salt or of the acid or acid salt to the neutral salt. From the values of $\alpha$ at one or more wavelengths, the apparent [5] dissociation constant, $K^*$, can then be calculated by the relationship

$$pK^*=pH-\log[\alpha/(1-\alpha)]. \tag{3}$$

At each step in the transformation, the calculated value of $\alpha$ should be the same for all wavelengths over the entire spectral range, if the reaction is merely one of dissociation. The best results, however, will be obtained at wavelengths in the middle of the absorption bands, and also in the regions where the transmittancy curves for the limiting ionic and molecular forms are widely separated. The spectral regions used for the calculations will therefore vary with the particular compound under investigation. Transmittancy values on steep slopes or near isosbestic points should be used with caution.

The values of $\alpha$ are averaged for several wavelengths. The average is then used for each intermediate stage of the ionization, and the $pK^*$ values are easily computed from eq 3 with the use of measured pH values of the buffered mixtures.

[5] This apparent dissociation constant has been termed the "incomplete" (unvollständig) dissociation constant by Bjerrum and Unmack [10]. It is defined by the equation $K^*=a_H(c_A/c_{HA})$, where $a$ and $c$ represent activity and concentration, respectively. It differs, therefore, from the classical constant, which involves the concentrations of reactants and products, and from the thermodynamic constant, which involves their activities.

## VI. PRESENTATION OF THE DATA

### 1. DISSOCIATION OF *p*-HYDROXYBENZOIC ACID

The spectral transmittancies are plotted as a function of wavelength in figures 1 and 2. The curves represent, progressively, the two stages in the dissociation of $4\times10^{-5}$-*M* *p*-hydroxybenzoic acid. The dissociation of the carboxyl group is represented by the six curves in figure 1. The second stage, that of the phenol group of the carboxylate salt, is shown by the 12 curves in figure 2. In the first series, the solutions used for the limiting forms and the intermediate steps

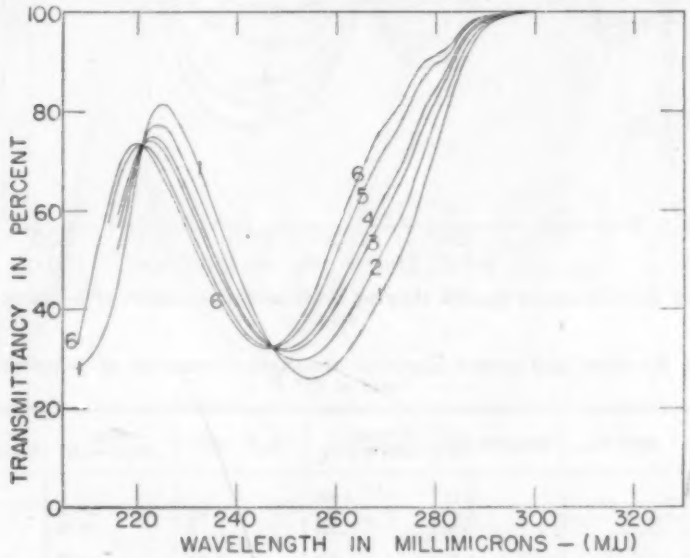


FIGURE 1.—*Ultraviolet spectra showing the first dissociation of p-hydroxybenzoic acid.*

in the transformation were 0.1-*M* hydrochloric acid (curve 1), a phosphate buffer (curve 6), and four intermediate acetate buffers (curves 2, 3, 4, 5). Although the latter were low in ionic strength, measurements could not be made below 216 m$\mu$, because the acetate itself cut out light at lower wavelengths. Many experiments at pH values near 7 were performed before the limiting curve, No. 6, was found. The intersecting curves 1 and 6 are not widely separated, and the slopes of the bands are rather steep. However, the values of $\alpha$ calculated at 2-m$\mu$ intervals between 254 and 286 m$\mu$, inclusive, are consistent. These 17 values for each step are averaged and given in table 2, column 3. The p$K^*$ values are then calculated by use of eq 3, and the measured pH values of each buffered solution. For the dissociation of the carboxyl group at 25° C, p$K^*$ is $4.5_1$.

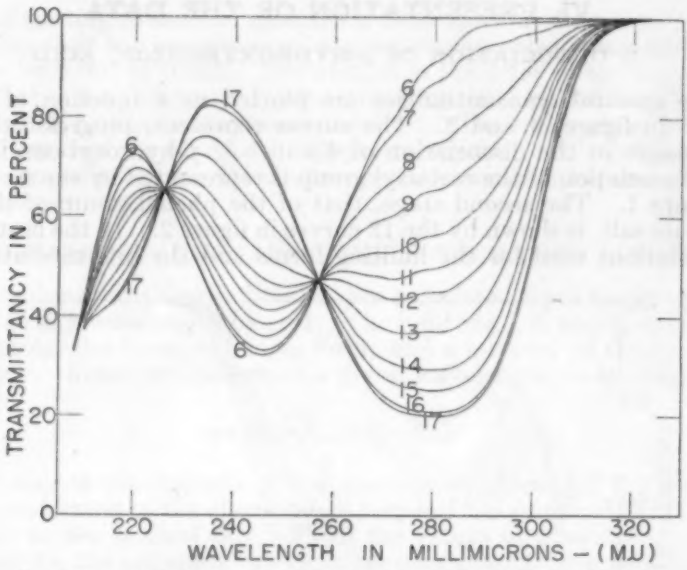


FIGURE 2.—*Ultraviolet spectra showing the second dissociation of p-hydroxybenzoic acid.*

TABLE 2.—*First and second apparent dissociation constants of p-hydroxybenzoic acid at 25° C*

| Figure 1, curve No. | Measured pH | Average $\alpha_1$ (λ254 to λ286) | $[\alpha_1/(1-\alpha_1)]$ | $\log_{10}[\alpha_1/(1-\alpha_1)]$ | $pK'_1=pH-\log_{10}[\alpha_1/(1-\alpha_1)]$ |
|---|---|---|---|---|---|
| 1 | 1.12 | 0.000 | | | |
| 2 | 4.17 | .302 | 0.432 | −0.36 | 4.5 |
| 3 | 4.58 | .529 | 1.123 | +.05 | 4.5 |
| 4 | 4.73 | .629 | 1.698 | +.23 | 4.5 |
| 5 | 5.32 | .876 | 7.091 | +.85 | 4.4 |
| 6 | 7.01 | 1.000 | | | |

| Figure 2, curve No. | Measured pH | Average $\alpha_2$ (λ264 to λ294) | $[\alpha_2/(1-\alpha_2)]$ | $\log_{10}[\alpha_2/(1-\alpha_2)]$ | $pK'_2=pH-\log_{10}[\alpha_2/(1-\alpha_2)]$ |
|---|---|---|---|---|---|
| 6 | 7.01 | 0.000 | | | |
| 7 | 7.96 | .031 | | | |
| 8 | 8.54 | .131 | 0.151 | −0.82 | 9.3 |
| 9 | 8.79 | .218 | .279 | −.55 | 9.3 |
| 10 | 8.99 | .317 | .465 | −.33 | 9.3 |
| 11 | 9.15 | .402 | .671 | −.17 | 9.3 |
| 12 | 9.28 | .468 | .879 | −.06 | 9.3 |
| 13 | 9.48 | .594 | 1.460 | +.16 | 9.3 |
| 14 | 9.79 | .745 | 2.925 | +.47 | 9.3 |
| 15 | 10.03 | .843 | 5.353 | +.73 | 9.3 |
| 16 | 10.84 | .969 | | | |
| 17 | 11.93 | 1.000 | | | |

The second series of curves, shown in figure 2, represents the second dissociation. The data for this series, curves 6 to 17, inclusive, were obtained by use of the same phosphate buffer used in the first series, several borate buffers, and $10^{-3}$-$M$ sodium hydroxide. The intersecting curves for the limiting forms, curves 6 and 17, have a wide spread and values of $\alpha$ were calculated at 17 wavelengths, 264 to 294

mμ, inclusive, at intervals of 2 mμ. The average α for each step is shown in column 3, table 2. For the second dissociation at 25° C, $pK^*_2$ is $9.3_3$.

### 2. DISSOCIATION OF METHYL *p*-HYDROXYBENZOATE

The partial neutralization of the phenol group of $4\times10^{-5}$-*M* methyl *p*-hydroxybenzoate was accomplished by the use of borate buffers. The molecular form was obtained in 0.1-*M* hydrochloric acid and the ionic form in $10^{-3}$-*M* sodium hydroxide. The values of α were calculated as above from the 12 curves as shown in figure 3.

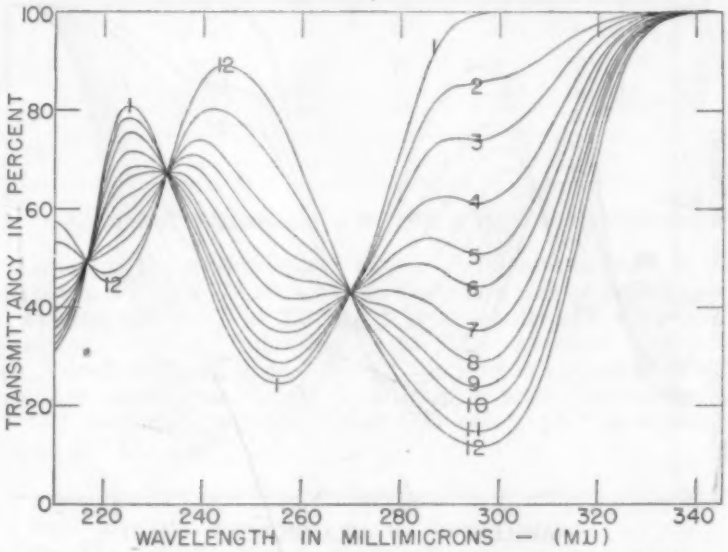


FIGURE 3.—*Ultraviolet spectra showing the dissociation of methyl p-hydroxybenzoate.*

The transmittancies at 2-mμ intervals between wavelengths 280 and 312 mμ, inclusive, were used. Averages of the α values obtained are given in table 3, column 3. An average $pK^*$ of $8.3_4$ at 25° C was obtained.

TABLE 3.—*Apparent dissociation constant of methyl p-hydroxybenzoate at 25° C*

| Figure 4, curve No. | Measured pH | Average α (λ280 to λ312) | $\alpha/(1-\alpha)$ | $\log_{10}[\alpha/(1-\alpha)]$ | $pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$ |
|---|---|---|---|---|---|
| 1 | 1.06 | 0.000 | | | |
| 2 | 7.22 | .070 | | | |
| 3 | 7.54 | .137 | 0.159 | −0.80 | 8.34 |
| 4 | 7.82 | .227 | .293 | −.53 | 8.35 |
| 5 | 8.01 | .314 | .457 | −.34 | 8.35 |
| 6 | 8.14 | .378 | .608 | −.22 | 8.36 |
| 7 | 8.33 | .485 | .941 | −.03 | 8.36 |
| 8 | 8.47 | .578 | 1.370 | +.14 | 8.33 |
| 9 | 8.62 | .667 | 2.007 | +.30 | 8.32 |
| 10 | 8.80 | .743 | 2.886 | +.48 | 8.34 |
| 11 | 9.20 | .889 | 7.993 | +.90 | 8.30 |
| 12 | 11.23 | 1.000 | | | |
| Average | | | | | 8.34 |

### 3. DISSOCIATION OF ETHYL *p*-HYDROXYBENZOATE

The ethyl ester of *p*-hydroxybenzoic acid was studied in somewhat more detail, with the use of three concentrations: $10^{-5}$ *M*, $2.5\times10^{-5}$ *M*, and $5\times10^{-5}$ *M*, in the 1-cm absorption cells. The series of curves for each concentration covered a different portion of the transmittancy scale, and thus a comprehensive analysis of the spectrophotometric data could be made. For brevity, however, the spectral data for only one concentration, namely, $5\times10^{-5}$ *M*, are shown in the 14 curves given in figure 4.

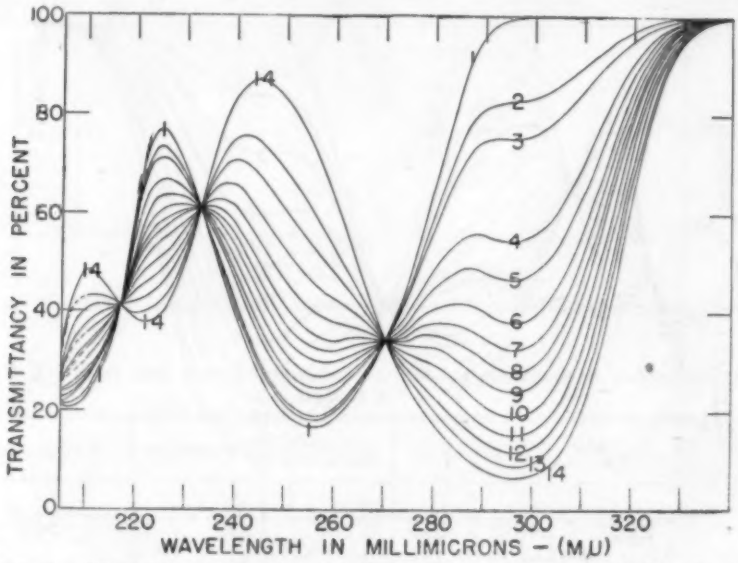


FIGURE 4.—*Ultraviolet spectra showing the dissociation of ethyl p-hydroxybenzoate*

For the limiting forms, 0.1-*M* hydrochloric acid and $10^{-3}$-*M* sodium hydroxide (curves 1 and 14) were used. For the 12 intermediate curves, Nos. 2 to 13, inclusive, borate buffers pH 7.3 to 9.2 were used. The values of $\alpha$ were calculated between wavelengths 280 to 312 mμ, inclusive, for each pH step. The average $\alpha$ for each series of the three concentrations is given in columns 3, 4, and 5 of table 4. Calculations were also made across the broader parts of the other two overlapping bands at the lower wavelengths, and the agreement was as good as experimental errors would allow. For the reasons previously stated, however, only the spectral data for the bands nearest the visible were used for final calculations. The average $pK^*$ for ethyl *p*-hydroxybenzoate at 25° C is $8.3_7$.

TABLE 4.—*Apparent dissociation constant of ethyl p-hydroxybenzoate at 25° C*

| Figure 4, curve No. | Measured pH | Average $a$'s (λ 280 to λ 312) | | | Average $[a/(1-a)]$ | $\log_{10}[a/(1-a)]$ | $pK^*=pH-\log_{10}[a/(1-a)]$ |
|---|---|---|---|---|---|---|---|
| | | $10^{-4}$ *M* | $2.5\times10^{-4}$ *M* | $5\times10^{-4}$ *M* | | | |
| 1 | 1.08 | 0.000 | 0.000 | 0.000 | | | |
| 2 | 7.27 | .068 | .067 | .068 | | | |
| 3 | 7.42 | .107 | .101 | .102 | 0.115 | −0.94 | 8.36 |
| 4 | 7.84 | .219 | .220 | .222 | .282 | −.55 | 8.39 |
| 5 | 7.94 | .287 | .279 | .280 | .392 | −.41 | 8.35 |
| 6 | 8.11 | .362 | .351 | .355 | .552 | −.26 | 8.37 |
| 7 | 8.23 | .416 | .417 | .411 | .709 | −.15 | 8.38 |
| 8 | 8.29 | .463 | .467 | .466 | .870 | −.06 | 8.35 |
| 9 | 8.42 | .522 | .516 | .521 | 1.082 | +.03 | 8.39 |
| 10 | 8.54 | .612 | .605 | .607 | 1.552 | +.19 | 8.35 |
| 11 | 8.71 | .698 | .688 | .695 | 2.264 | +.35 | 8.36 |
| 12 | 8.92 | .787 | .785 | .786 | 3.669 | +.56 | 8.36 |
| 13 | 9.21 | .886 | .874 | .884 | 7.446 | +.87 | 8.34 |
| 14 | 11.24 | 1.000 | 1.000 | 1.000 | | | |
| Average | | | | | | | 8.37 |

## 4. DISSOCIATION OF *n*-BUTYL *p*-HYDROXYBENZOATE

Although the *n*-butyl ester of *p*-hydroxybenzoic acid is difficultly soluble in water, a $5\times10^{-4}$-*M* stock solution was prepared. Solutions containing the ester in $2.5\times10^{-5}$-*M* concentration were used for the spectrophotometric measurements. The spectral transmittancies are plotted in figure 5, and the calculations are given in table 5. The solutions used were 0.1-*M* hydrochloric acid, borate buffers, and $10^{-3}$-*M* sodium hydroxide. For this ester, $pK^*$ was found to be $8.3_4$ at 25° C.

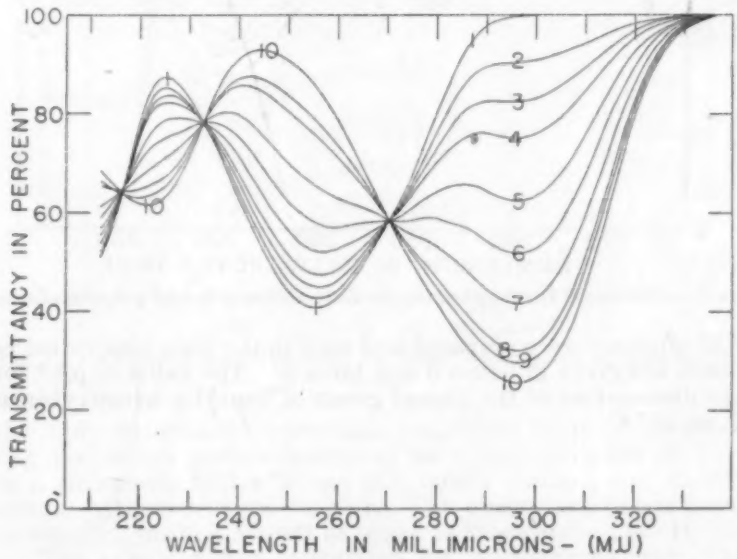


FIGURE 5.—*Ultraviolet spectra showing the dissociation of n-butyl p-hydroxybenzoate.*

TABLE 5.—*Apparent dissociation constant of n-butyl p-hydroxybenzoate at 25° C*

| Figure 5, curve No. | Measured pH | Average $\alpha$ ($\lambda$282 to $\lambda$310) | $[\alpha/(1-\alpha)]$ | $\log_{10}[\alpha/(1-\alpha)]$ | $pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$ |
|---|---|---|---|---|---|
| 1 | 1.12 | 0.000 | | | |
| 2 | 7.28 | .071 | 0.077 | −1.11 | 8.39 |
| 3 | 7.60 | .139 | .161 | −0.79 | 8.39 |
| 4 | 7.81 | .207 | .261 | −.58 | 8.39 |
| 5 | 8.11 | .342 | .521 | −.28 | 8.39 |
| 6 | 8.27 | .482 | .930 | −.03 | 8.30 |
| 7 | 8.52 | .642 | 1.794 | +.25 | 8.27 |
| 8 | 9.00 | .832 | 4.942 | +.69 | 8.31 |
| 9 | 9.23 | .892 | 8.294 | +.92 | 8.31 |
| 10 | 11.56 | 1.000 | | | |
| Average | | | | | 8.34 |

## 5. DISSOCIATION OF BENZYL *p*-HYDROXYBENZOATE

Benzyl *p*-hydroxybenzoate is also very slightly soluble in water. A stock solution, $10^{-4}$ *M* in the ester, was made up, from which

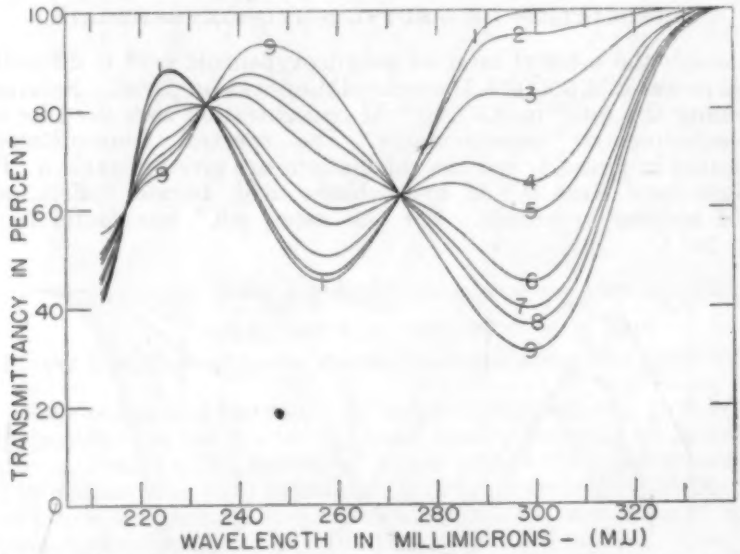


FIGURE 6.—*Ultraviolet spectra showing the dissociation of benzyl p-hydroxybenzoate.*

$10^{-5}$-*M* solutions were prepared and used in the 2-cm absorption cells. The data are given in figure 6 and table 6. The value of $pK^*$ found or the dissociation of the phenol group of benzyl p-hydroxybenzoate s $8.2_8$ at 25° C.

TABLE 6.—*Apparent dissociation constant of benzyl p-hydrozybenzoate at 25° C*

| Figure 6, curve No. | Measured pH | Average $\alpha$ ($\lambda$282 to $\lambda$310) | $[\alpha/(1-\alpha)]$ | $\log_{10}[\alpha/(1-\alpha)]$ | $pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$ |
|---|---|---|---|---|---|
| 1 | 1.03 | 0.000 | | | |
| 2 | 6.91 | .039 | 0.040 | −1.39 | 8.30 |
| 3 | 7.55 | .156 | .185 | −0.73 | 8.28 |
| 4 | 8.05 | .359 | .561 | −.25 | 8.30 |
| 5 | 8.21 | .445 | .803 | −.10 | 8.31 |
| 6 | 8.57 | .676 | 2.089 | +.32 | 8.25 |
| 7 | 8.83 | .783 | 3.600 | +.56 | 8.27 |
| 8 | 9.04 | .855 | 5.901 | +.77 | 8.27 |
| 9 | 11.63 | 1.000 | | | |
| Average | | | | | 8.28 |

## 6. DISSOCIATION OF POTASSIUM *p*-PHENOLSULFONATE

Potassium *p*-phenolsulfonate is fairly soluble in water. Preliminary curves were given for the primary and secondary salts in an earlier publication [1].

The spectral transmittancy curves, shown in figure 7, represent some of the steps in the transformation of the *p*-phenosulfonic acid

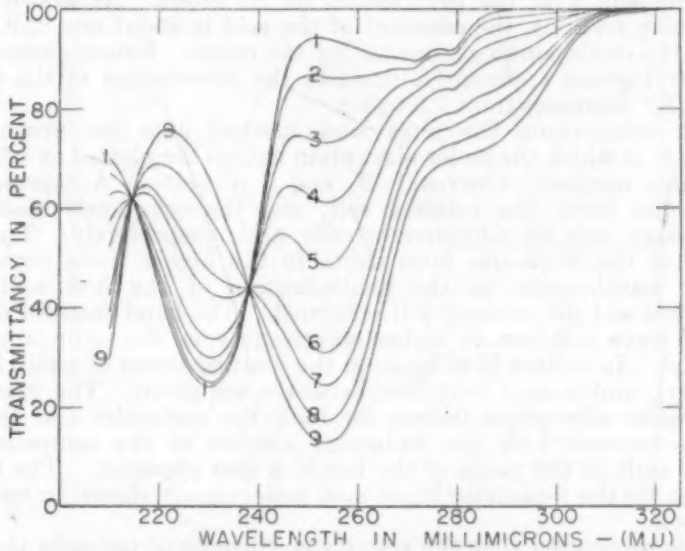


FIGURE 7.—*Ultraviolet spectra showing the second dissociation of p-phenolsulfonic acid.*

to the fully neutralized secondary potassium salt. Solutions containing potassium *p*-phenolsulfonate at a concentration of $5\times10^{-5}$ *M* in a phosphate buffer, in several borate buffers, and in $10^{-2}$-*M* potassium hydroxide were studied. The absorption bands occur at lower wavelengths and are not as broad as those of the hydroxybenzoates. The $\alpha$ values were calculated for wavelengths from 244 to 264 m$\mu$, inclusive, and the averages of the different values at each pH are given in table 7. Calculations were made as described previously. A $pK^*$ of $8.9_0$ at 25° C was obtained.

TABLE 7.—*Apparent dissociation constant of potassium-p-phenolsulfonate at 25° C*

| Figure 7, Curve No. | Measured pH | $\alpha$ $10^{-4}$ $M$ λ244 to λ264 | $\alpha$ $5\times10^{-4}$ $M$ λ244 to λ264 | Average $[\alpha/(1-\alpha)]$ | $\log_{10}$ $[\alpha/(1-\alpha)]$ | $pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$ |
|---|---|---|---|---|---|---|
| 1 | 1.08 | 0.0000 | 0.0000 | | | |
| 2 | 7.38 | .045 | .043 | | | |
| Not drawn | 7.66 | .077 | .076 | | | |
| Do | 7.85 | .106 | .104 | 0.117 | −0.93 | 8.78 |
| 3 | 8.05 | .124 | .125 | .143 | −.85 | 8.90 |
| 4 | 8.33 | .212 | .214 | .271 | −.57 | 8.90 |
| 5 | 8.57 | .325 | .329 | .486 | −.31 | 8.88 |
| 6 | 8.98 | .556 | .552 | 1.243 | +.09 | 8.89 |
| 7 | 9.20 | .668 | .670 | 1.623 | +.30 | 8.90 |
| 8 | 9.66 | .848 | .844 | 5.489 | +.74 | 8.92 |
| 9 | 11.20 | 1.000 | 1.000 | | | |

## VII. DISCUSSION

The dissociation of the esters of *p*-hydroxybenzoic acid and the dissociation of the unsubstituted acid from spectrophotometric studies are demonstrated in the foregoing data. It is of interest to compare the value of the apparent second dissociation constant of *p*-hydroxybenzoic acid with the $pK^*$ values for its esters. As shown in the foregoing sections, the constant of the acid is about one unit higher than the corresponding constant for the esters. Esterification of the carboxyl group apparently increases the dissociation of the phenol, and $pK^*$ decreases from 9.3 to 8.3.

For comparison, the ultraviolet spectral data are presented in figure 8, in which the molar absorption indices are plotted as a function of wave number. Curves 1, 2, and 3 in section A represent the molecular form, the primary salt, and the completely neutralized secondary salt of *p*-hydroxybenzoic acid, respectively. The main band of the molecular form shifts to the higher wave numbers or lower wavelengths, as the neutralization of the first acid group proceeds and the primary salt is formed. The band then shifts to the lower wave numbers or higher wavelengths, as the secondary salt is formed. In section B of figure 8, the limiting forms of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate are given. The maxima in the molar absorption indices for both the molecular and the ionic forms increase with the molecular weights of the compounds. A slight shift in the peaks of the bands is also apparent. The limiting curves for the *p*-phenolsulfonic acid molecule are shown in section C, figure 8.

It is recognized that the activity coefficients of not only the buffer ions but also of the compounds themselves must be considered in order to determine the thermodynamic ionization constants. All the buffers were dilute and of practically the same ionic strengths. It is not feasible at present to make a more extensive study with buffers of many different concentrations. When a wide range of buffers of accurately known pH is available and further refinements in control of temperature of the spectrophotometric absorption cells have been made, the measurements can be extended to furnish data from which calculations of the true thermodynamic constants can be made.

If measurements of the type described here were made with buffers of widely different concentrations, it would be possible to determine

$pK_a$, the negative of the logarithm of the thermodynamic dissociation constant, by the extrapolation of measured values of $pK^*$, to zero ionic strength, where the activity-coefficient correction becomes zero by definition and the apparent and true dissociation constants are identical. In general, it can be expected that $pK_a$ for the second dis-

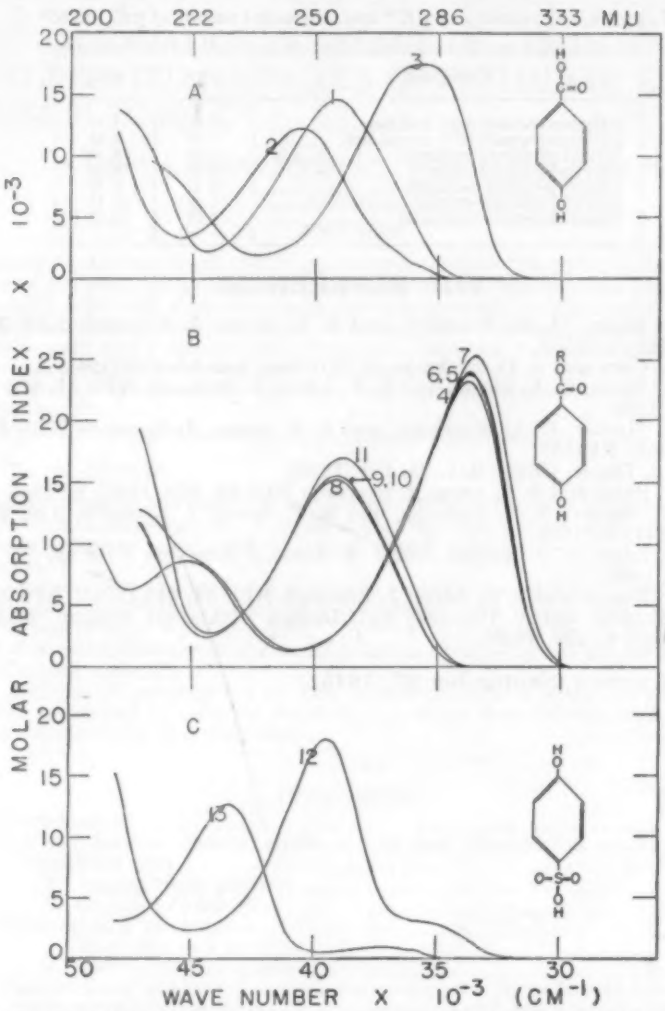


FIGURE 8.—*Limiting spectral absorption curves for p-hydroxybenzoic acid, A, menthyl, ethyl, n-butyl, and benzyl p-phydroxybenzoate, B and potassium p-phenolsulfonate, C.*

sociation of *p*-hydroxybenzoic acid would be about 0.18 higher than the $pK^*$ value obtained at an ionic strength of 0.02. For the same ionic strength, the $pK_a$ for the first dissociation of this acid and for the dissociation of the esters would be about 0.06 higher than the $pK^*$ values listed. Inasmuch as borate buffers approximately 0.01 in ionic strength were used, for the most part, in obtaining $pK^*$ for potassium

*p*-phenolsulfonate, the correction for activity coefficients amount to about 0.13 unit. The value of $pK_a$ thus becomes 9.03, or slightly lower than 9.053 found by emf methods at 25° C [3]. The $pK^*$ values found by spectrophotometric methods are listed in table 8, together with the estimated values for $pK_a$.

TABLE 8.—*Summary of* $pK^*$ *and estimated values of* $pK_a$ *at 25° C*

| Compound | $pK^*$ | $pK_a$ |
|---|---|---|
| *p*-Hydroxybenzoic acid, first step | 4.51 | 4.57 |
| *p*-Hydroxybenzoic acid, second step | 9.33 | 9.46 |
| Methyl *p*-hydroxybenzoate | 8.34 | 8.47 |
| Ethyl *p*-hydroxybenzoate | 8.37 | 8.50 |
| *n*-Butyl *p*-hydroxybenzoate | 8.34 | 8.47 |
| Benzyl *p*-hydroxybenzoate | 8.28 | 8.41 |
| Potassium *p*-phenolsulfonate | 8.90 | 9.03 |

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# FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID AND RELATED pH VALUES OF PHTHALATE BUFFERS FROM 0° TO 60° C

By Walter J. Hamer, Gladys D. Pinching and S. F. Acree

**ABSTRACT**

Measurements were made at 5-degree intervals from 0° to 60° C of the potential difference between hydrogen electrodes and silver–silver-chloride electrodes in 45 aqueous solutions that contained various amounts of *o*-phthalic acid, acid potassium phthalate, and potassium chloride. The first dissociation constant of *o*-phthalic acid and related thermodynamic quantities were evaluated, and pH values were assigned to each of the 45 solutions.

The equation obtained for the first dissociation constant as a function of temperature is

$$\log K_1 = -561.57/T + 1.2843 - 0.0078833T,$$

where $T = t°C + 273.16$.

The pH values of the solutions range from 2.70 to 3.26 and vary only slightly with changes in temperature. The solutions have good buffer capacity and may be readily prepared from pure materials. Each solution is suited for use as a pH standard.

The separation of the carboxyl groups in *o*-phthalic acid was found to be 1.66 A by means of an equation relating this distance with the ratio of the two dissociation constants of *o*-phthalic acid. This value is higher than 1.53 A obtained from X-ray measurements of the carbon-carbon distance in the diamond and 1.43 in the benzene molecule.

The problem of convergence or lack of convergence of apparent dissociation constants calculated by different methods to a single thermodynamic value in the limit of infinite dilution is discussed.

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## I. INTRODUCTION

A previous publication [1] [1] gave values of the second dissociation constant of *o*-phthalic acid, of related thermodynamic quantities,

[1] Figures in brackets indicate the literature references at the end of this paper.

and of the pH values of solutions containing acid potassium phthalate and dipotassium phthalate with or without potassium chloride at intervals of 5° from 0° to 60° C. There are now presented results of measurements over the same range of temperature of galvanic cells without liquid junction and comprised of hydrogen and silver–silver-chloride electrodes for the determination of the first dissociation constant of *o*-phthalic acid, of related thermodynamic quantities, and of the pH values of solutions containing acid potassium phthalate, *o*-phthalic acid, and potassium chloride. Both constants are needed for the calculation of the pH values of solutions of acid potassium phthalate by the equation

$$m_{\mathrm{H}}^3+[a+(K_1 f_{\mathrm{H_2Ph}})/(f_{\mathrm{H}} f_{\mathrm{HPh}})]m_{\mathrm{H}}^2+[(K_1K_2 f_{\mathrm{H_2Ph}})/(f_{\mathrm{H}}^2 f_{\mathrm{Ph}})]m_{\mathrm{H}}- (aK_1K_2 f_{\mathrm{H_2Ph}})/(f_{\mathrm{H}}^2 f_{\mathrm{Ph}})=0, \quad (1)$$

where $K_1$ and $K_2$ are, respectively, the first and second dissociation constants of *o*-phthalic acid, $a$ is the stoichiometric concentration of acid potassium phthalate, $m_{\mathrm{H}}$ is the hydrogen-ion concentration, and $f$ represents the activity coefficient of the species denoted by subscripts.[2]

## II. METHOD FOR THE DETERMINATION OF THE FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

### 1. APPROXIMATE METHOD

In the determination of the first dissociation constant of *o*-phthalic acid by the electromotive-force method, measurements are made of the emf of the galvanic cell

$$\mathrm{Pd,\ H_2(g)|H_2Ph}(m_1),\ \mathrm{KHPh}\ (m_2),\ \mathrm{KCl}\ (m_3)|\mathrm{AgCl(s)|Ag(s)}$$

for a series of solutions of different molalities, $m_1$, $m_2$, and $m_3$ and of various ratios, $\mathrm{H_2Ph/KHPh}$, wherein the hydrogen and silver–silver-chloride electrodes are reversible, respectively, to hydrogen and chloride ions or their hydrates. The addition of the chloride is therefore a prerequisite for the use of silver-silver-chloride electrodes in such mixtures.

The calculation of the constant depends upon the equation

$$E=E^\circ-(RT/F)\ln(a_{\mathrm{H}}a_{\mathrm{Cl}})=E^\circ-(RT/F)\ln a_{\mathrm{H}}-(RT/F)\ln(f_{\mathrm{Cl}}m_{\mathrm{Cl}}), \quad (2)$$

which relates the emf of the cell, $E$, with the activities of the hydrogen and chloride ions, and upon the mass-action expression,

$$K_1=(a_{\mathrm{H}}a_{\mathrm{HPh}})/(a_{\mathrm{H_2Ph}})=(a_{\mathrm{H}}f_{\mathrm{HPh}}m_{\mathrm{HPh}})/(f_{\mathrm{H_2Ph}}m_{\mathrm{H_2Ph}}), \quad (3)$$

which defines the dynamic equilibrium between the ions and undissociated *o*-phthalic acid for the process $\mathrm{H_2Ph}\rightleftharpoons\mathrm{H^+}+\mathrm{HPh^-}$. $E^\circ$ is the potential of the silver–silver-chloride electrode for unit activity of hydrochloric acid; $a$, $f$, and $m$ are the activity, activity coefficient, and molality of the species denoted by subscripts; and $R$, $T$, and $F$ have their usual significance.

[2] The symbols $\mathrm{H_2Ph}$, $\mathrm{HPh}$, and $\mathrm{Ph}$ are used to designate, respectively, *o*-phthalic acid, acid phthalate ion, and diphthalate ion for convenience. The charges on the ions have been omitted.

In the above two equations, $E$, $E^\circ$, $m_{HPh}$, $m_{H_2Ph}$, $m_{Cl}$, $R$, $T$, and $F$ are known quantities, whereas $a_H$ and the other activities and activity coefficients are unknown quantities. The former unknown, ($a_H$,) may be eliminated by combination of eq 2 and 3, which gives

$$[(E-E^\circ)/(2.3026RT/F)+\log (m_3m_1/m_2)]+\log (f_{Cl}f_{H_2Ph}/f_{HPh})= -\log K_1=pK_1 \quad (4)$$

upon substitution of $m_1$, $m_2$, and $m_3$, respectively, for $H_2Ph$, $HPh^-$, and $Cl^-$. This equation still contains one unknown quantity—the third term on the left side, which is made up of the activity coefficients of one neutral molecule and two ions. The activity coefficient of the neutral molecule may be assigned a value of unity, as is customary. For example, Scatchard, Hamer, and Wood [2] by means of isotonic measurements obtained values of 1.0146, 0.9918, and 1.0026, respectively, for the activity coefficient of sucrose, urea, and glycerol of 0.1 molality. Extrapolation of their data gives values of 1.0029, 0.9984, and 1.0005 or an average value of 1.0006 for a 0.018-molal solution, the highest molality of *o*-phthalic acid used in this work. Hence, the assumption that the activity coefficient of undissociated *o*-phthalic acid is unity does not introduce an appreciable error in the final results. Even if the ions in solution do not conform to the laws of perfect solutes, the value of the third term should approach zero, as the values of the activity coefficients of the chloride and acid phthalate ions on a mole-fraction basis give the magnitude of the deviations of ions or molecules from the perfect state and should be practically equal. Only at infinite dilution do ions possess the characteristics of ideal solutes. Hence if values of the term in brackets, designated as $pK_1'$, for decreasing values of $(m_3m_1/m_2)$ are plotted against the ionic strength, values of $pK_1$ are obtained by extrapolation to zero ionic strength.

## 2. COMPLETE METHOD

In the foregoing it was assumed that the ratio, $m_1/m_2$, may be determined from the stoichiometrical molalities of *o*-phthalic acid and acid potassium phthalate. However, owing to various ionic equilibria, this is not strictly true and corrections must therefore be made.

In a mixture of *o*-phthalic acid with its acid salt, the essential equilibria are

$$H_2Ph \rightleftharpoons H^+ + HPh^- \quad (5)$$

and

$$HPh^- \rightleftharpoons H^+ + Ph^=, \quad (6)$$

which upon subtraction give

$$2\,HPh^- \rightleftharpoons H_2Ph + Ph^=. \quad (7)$$

In each case, the ions and molecules are in dynamic equilibrium defined by the mass-action expressions. These give, respectively, for processes 6 and 7

$$K_2=(a_Ha_{Ph})/a_{HPh}=(a_Hf_{Ph}m_{Ph})/(f_{HPh}m_{HPh}) \quad (8)$$

and

$$K_2/K_1=(a_{Ph}a_{H_2Ph})/a^2_{HPh}=(f_{Ph}f_{H_2Ph}m_{Ph}m_{H_2Ph})/(f_{HPh}m_{HPh})^2. \quad (9)$$

The expression for process 5 is given by eq 3, where the terms have the same significance as given above.

As a result of these equilibria, eq 10 applies to a solution composed of $H_2Ph$ of molality of $m_1$ and of KHPh of a molality of $m_2$

$$m_{H_2Ph}=m_1-m_H+m_{Ph} \tag{10}$$

as $H_2Ph$ is removed to form hydrogen ions in reaction 5 and is formed in reaction 7 in an amount equivalent to $Ph^=$. Furthermore, eq 11 holds

$$m_{HPh}=m_2+m_H-2m_{Ph} \tag{11}$$

as $HPh^-$ is formed in reaction 5 and removed in reaction 7 in amounts equivalent, respectively, to $H^+$ and $2Ph^=$. Consequently, the stoichiometrical molalities of $H_2Ph$ and KHPh will be altered,[3] and a solution containing them will also contain a quantity of $Ph^=$ ions. However, if $K_2/K_1$ is less than about $10^{-3}$ the tendency of reaction 7 to take place from left to right will be small and $m_{Ph}$ in eq 10 and 11 may be neglected, leaving only corrections for $m_H$.

The values of $m_H$ may be obtained from the emf of the cell as follows [3]: Rearrangement of eq 2 gives

$$(E-E^\circ)/(2.3026RT/F)+\log m_{Cl}+\log f_H f_{Cl}=-\log m_H. \tag{12}$$

Values of $\log f_H f_{Cl}$ may be obtained by either (1) the limiting law of Debye and Hückel [4], $-\log f_H f_{Cl}=2A\sqrt{\mu}$; (2) the Guggenheim equation [5], $-\log f_H f_{Cl}=2A\sqrt{\mu}/(1+\sqrt{\mu})$; (3) the extended Debye-Hückel equation [4] $-\log f_H f_{Cl}=2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$; or by (4) the Hückel extension of the Debye-Hückel equation [6], $-\log f_H f_{Cl}=2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu$. Thus four different values of $m_H$ may be obtained, depending upon which equation is used to evaluate $-\log f_H f_{Cl}$. The four values of $m_H$ agree more closely for dilute solutions, as the four expressions for the activity coefficient become equivalent at extreme dilutions. As $\mu=m_2+m_3+m_H$ each calculation involves a successive approximation. First, $\mu$ is taken equal to $m_2+m_3$, and a provisional value of $m_H$ is calculated by eq 12 and one of the Hückel equations. With this value of $m_H$ a new $\mu$ is determined from the relation $\mu=m_2+m_3+m_H$, and so on until self-consistent values of $\mu$ and $m_H$ are obtained.[4]

From data reported in the literature [7] for *o*-phthalic acid, $K_2/K_1$ is about $3\times10^{-3}$, which exceeds the condition postulated for the neglect of $m_{Ph}$ in eqs 10 and 11. Therefore, corrections for $Ph^=$, sometimes called the "overlapping" corrections because $H_2Ph$ and $HPh^-$ are titrated simultaneously, become necessary, even though they are small.

The corrections may be obtained as follows by methods described in a previous paper [1]. If $a$ equals the molality of the acid and $b$ the molality of added alkali, then for any mixture of the two

$$a=m_{H_2Ph}+m_{HPh}+m_{Ph}, \tag{13}$$

$$b+m_H=m_{HPh}+2m_{Ph}. \tag{14}$$

[3] The concentrations of $H_2Ph$ may be determined directly by partition methods if proper standard states are chosen for each solvent. For a determination of the concentration of undissociated molecules by the spectrophotometric method, see reference [26].

[4] This successive approximation involves the use of two equations, eq 12 and the equation $\mu=m_2+m_3+m_H$. Actually, $\mu=m_2+m_3+m_H-m_{Ph}$, where values of $m_{Ph}$ are given by eq 15. Complete calculations of $\mu$ therefore involves successive approximations by using three equations (see complete treatment).

By the use of these equations and eq 3 and 8, eq 15,

$$m_{Ph}=\frac{[(K_1 f_{H_2Ph})/(f_H f_{HPh})+m_H](b+m_H)-(aK_1 f_{H_2Ph})/(f_H f_{HPh})}{2m_H+(K_1 f_{H_2Ph})/(f_H f_{HPh})}, \quad (15)$$

results if eq 16,

$$m_H^3+[a+(K_1 f_{H_2Ph})/(f_H f_{HPh})]m_H^2+[(K_1K_2 f_{H_2Ph})/(f_H^2 f_{Ph})+(bK_1 f_{H_2Ph})/(f_H f_{HPh})-(aK_1 f_{H_2Ph})/(f_H f_{HPh})]m_H+[(K_1K_2 f_{H_2Ph})/(f_H^2 f_{Ph})](b-2a)=0, \quad (16)$$

obtained by the elimination of $m_{H_2Ph}$, $m_{HPh}$, and $m_{Ph}$ in eq 3, 8, 10, and 11, is satisfied for the solutions of any composition and concentration. However, solution of eq 15 requires a knowledge of $m_H$, the activity coefficients, $K_1$, and $K_2$. Values of $m_H$ are obtained by eq 12 discussed above. Values of the activity coefficients are obtained by the Debye-Hückel equations given above. Values of $K_2$ are taken from a previous publication by Hamer and Acree [1]. Values of $K_1$ used first are those obtained by the simplified procedure described above. After values of $m_{Ph}$ are calculated in this way, they are used in eq 10 and 11 to calculate new values of the molality of $H_2Ph$ and $HPh^-$. These latter values are then used to calculate new values of $\mu$ and $K_1$, and the arithmetical procedure is continued until self-consistent values of $K_1$, $\mu$, and $m_{Ph}$ are obtained (see footnote 4 for calculations of values of ionic strength). The final values of $pK_1$ are then obtained by the equation

$$(E-E^\circ)/(2.3026RT/F)+\log [m_3(m_1-m_H+m_{Ph})/(m_2+m_H-2m_{Ph})]+\log (f_{Cl}/f_{HPh})=-\log K_1=pK_1, \quad (17)$$

where the same Debye-Hückel expression is used for the term $\log (f_{Cl}/f_{HPh})$ as was employed to calculate values of $m_H$ and $m_{Ph}$.

## III. EXPERIMENTAL PROCEDURES

### 1. MATERIALS AND SOLUTIONS

The solutions used in this investigation were prepared in a $CO_2$-free atmosphere from known weights of stock solutions containing *o*-phthalic acid, acid potassium phthalate, and potassium chloride by dilution with known weights of conductivity water having a specific conductance of 0.6 to $1.0\times10^{-6}$ mho. Two different stock solutions were used. The stock solutions for series I, II, III, and IV were prepared from known weights of dry *o*-phthalic acid, dry acid potassium phthalate, dry potassium chloride, and conductivity water. The stock solution for series V was prepared by the addition of the requisite amount of dry acid potassium phthalate to a standardized solution of hydrochloric acid.

Solutions containing more than 0.018 mole of *o*-phthalic acid and acid potassium phthalate were not used, as crystals of phthalic acid separate from more concentrated solutions at the lower temperatures. After the solutions were prepared, they were deaerated by means of hydrogen gas, and corrections were made for loss of water from the solutions and the differences between the densities of hydrogen and air.

Resublimed phthalic anhydride that gave less than 0.002-percent ash when ignited was boiled with distilled water. The resulting *o*-

phthalic acid was then recrystallized three times from distilled water and extracted with benzene in a Soxhlet extractor. After distillation of the benzene, the acid was boiled with water to remove any traces of anhydride that may have been formed and was finally recrystallized from water. After air-drying, the crystals were lightly ground in an agate mortar and dried in vacuum at room temperature over anhydrous magnesium perchlorate. Two lots of the acid were prepared and the purity of each was tested by weight titration in $CO_2$-free atmosphere against $CO_2$-free sodium hydroxide standardized against acid potassium phthalate, National Bureau of Standards Standard Sample 84a, phenolphthalein solution, being used as the indicator. The purity of one lot of the acid as indicated by the titrations was 100 percent and that of the other was 99.85 percent. However, when samples of the second lot were carefully ground for a second time and redried in vacuum at room temperature over anhydrous magnesium perchlorate the purity rose to 100 percent. Hence, it was assumed that the impurity was water entrapped in the crystals, and allowance was made for it in the preparation of the solutions.

The acid potassium phthalate was NBS Standard Sample 84a having a certified purity of 100.00 percent determined by titration. It was dried according to the directions given in the Bureau certificate and was allowed to cool in a desiccator, concentrated sulfuric acid being used as the desiccant.

The potassium chloride was recrystallized twice from conductivity water and then thrice from 95-percent ethanol to remove the last traces of bromide. It was dried for 10 hours at 110° C and allowed to cool in a desiccator over concentrated sulfuric acid.

The hydrochloric acid solution was prepared by dissolving in conductivity water the hydrogen chloride gas formed by the action of concentrated sulfuric acid on lumps of fused ammonium chloride. The strength of the acid was determined by weight titration with a solution of carbonate-free sodium hydroxide standardized against acid potassium phthalate, NBS Standard Sample 84a. Phenolphthalein solution was used as the indicator in each case. Determinations agreed within 0.04 percent.

### 2. ELECTRODES AND APPARATUS

Hydrogen electrodes of platinum foil covered with palladium were prepared as described in another paper [10]. Electrodes of this type do not catalyze the reduction of phthalates, and they function reversibly for well over 100 hours.

Silver–silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials by the method previously described [9]. They were aged sufficiently to bring them to a stable state [10, 11].

The details of the apparatus employed in these studies, including the cells, bubble tubes, thermostat, and the emf recording instruments have been described by Hamer and Acree [9]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at all the temperatures, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell. The emf measurements were corrected in the usual manner to 1 atmosphere of hydrogen pressure.

## IV. CALCULATION OF THE FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

The electromotive forces obtained at intervals of 5 degrees from 0° to 60° C in the five series of experiments on different ratios, $H_2Ph$/KHPh, and different chloride ratios, KCl/KHPh, designated as series I to V, are given in tables 1 to 5. The compositions of the different solutions are defined in terms of the molality of acid potassium phthalate given in column 1 (tables 3 and 4 excepted) and the buffer ratio given at the top of each table. In series I to V the solutions had a buffer ratio, respectively, of 1.5, 2.0, 1.0, 2.0, and 1.5 and a KCl/KHPh ratio, respectively, of 1.0, 1.0, variable ratio, variable ratio, and 1.5. In series I, four measurements marked by a superscript *a* were for a buffer ratio of 1.5063 and a KCl/KHPh ratio of unity.

TABLE 1.—*Electromotive forces of galvanic cells with hydrogen and silver–silver chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES 1 {MOLALITY OF o-PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE, MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE

| Solution number | Molality of KHPh | Temperature in degrees centigrade | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 |
| | *Moles of solute per 1,000 g of water* | E | E | E | E | E | E |
| I 1 | 0.0018357 | 0.55244 | 0.55577 | 0.55904 | 0.56217 | 0.56519 | 0.56812 |
| I 2 | .0019071 | .55119 | .55444 | .55771 | .56076 | .56382 | .56672 |
| I 3 | .0027658 | .53897 | .54204 | .54516 | .54794 | .55080 | .55352 |
| I 4 | .0034165 | .53218 | .53520 | .53813 | .54090 | .54359 | .54626 |
| I 5 | .0039521 | .52765 | .53062 | .53348 | .53600 | .53880 | .54131 |
| I 6 | [a].0040518 | .52681 | .52979 | .53258 | .53523 | .53784 | .54026 |
| I 7 | .0046056 | .52299 | .52589 | .52871 | .53121 | .53372 | .53619 |
| I 8 | .0047953 | .52182 | .52455 | .52734 | .52993 | .53244 | .53493 |
| I 9 | .0068606 | .51109 | .51378 | .51631 | .51869 | .52105 | .52332 |
| I 10 | .0079547 | .50686 | .50935 | .51196 | .51418 | .51645 | .51868 |
| I 11 | .0081020 | .50628 | .50888 | .51134 | .51361 | .51591 | .51807 |
| I 12 | [a].011058 | .49738 | .49981 | .50211 | .50426 | .50637 | .50841 |
| I 13 | [a].011799 | .49558 | .49800 | .50025 | .50238 | .50445 | .50644 |
| I 14 | [a].011913 | .49533 | .49772 | .49995 | .50207 | .50418 | .50612 |
| I 15 | .012000 | .49522 | .49760 | .49983 | .50194 | .50401 | .50606 |

| Solution number | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| | E | E | E | E | E | E | E |
| I 1 | 0.57102 | 0.57362 | 0.57620 | 0.57857 | 0.58103 | 0.58337 | 0.58563 |
| I 2 | .56949 | .57213 | .57474 | .57709 | .57942 | .58179 | .58392 |
| I 3 | .55613 | .55857 | .56098 | .56309 | .56529 | .56749 | .56956 |
| I 4 | .54876 | .55108 | .55339 | .55540 | .55751 | .55966 | .56154 |
| I 5 | .54373 | .54605 | .54828 | .55020 | .55222 | .55428 | .55618 |
| I 6 | .54279 | .54501 | .54728 | .54917 | .55126 | .55329 | .55514 |
| I 7 | .53852 | .54081 | .54287 | .54488 | .54678 | .54873 | .55059 |
| I 8 | .53724 | .53939 | .54153 | .54342 | .54536 | .54738 | .54920 |
| I 9 | .52544 | .52752 | .52942 | .53123 | .53297 | .53481 | .53650 |
| I 10 | .52077 | .52272 | .52457 | .52627 | .52805 | .52979 | .53142 |
| I 11 | .52018 | .52212 | .52390 | .52568 | .52735 | .52918 | .53077 |
| I 12 | .51038 | .51216 | .51388 | .51544 | .51704 | .51866 | .52015 |
| I 13 | .50839 | .51019 | .51182 | .51343 | .51496 | .51656 | .51798 |
| I 14 | .50806 | .50989 | .51155 | .51309 | .51458 | .51619 | .51763 |
| I 15 | .50800 | .50971 | .51142 | .51292 | .51447 | .51606 | .51750 |

[a] Molality of *o*-phthalic acid=1.5063×molality of acid potassium phthalate and molality of potassium chloride=molality of acid potassium phthalate.

TABLE 2.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES II. {MOLALITY OF o-PHTHALIC ACID = 2.0000 × MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE = MOLALITY OF ACID POTASSIUM PHTHALATE.

| Solution number | Molality of KHPh | Temperature in degrees centigrade | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 |
| | *Moles of solute per 1,000 g of water* | E | E | E | E | E | E |
| II 1 | 0.0008187 | 0.57528 | 0.57902 | 0.58207 | 0.58616 | 0.58954 | 0.59284 |
| II 2 | .0014005 | .55027 | .55976 | .56299 | .56618 | .56920 | .57227 |
| II 3 | .0014548 | .55492 | .55837 | .56166 | .56479 | .56784 | .57085 |
| II 4 | .0023517 | .53888 | .54194 | .54504 | .54783 | .55061 | .55334 |
| II 5 | .0024641 | .53721 | .54037 | .54336 | .54622 | .54900 | .55170 |
| II 6 | .0031025 | .52996 | .53279 | .53571 | .53839 | .54105 | .54359 |
| II 7 | .0036743 | .52441 | .52738 | .53011 | .53273 | .53531 | .53779 |
| II 8 | .0050000 | .51490 | .51763 | .52025 | .52272 | .52513 | .52745 |
| II 9 | .0071782 | .50413 | .50661 | .50901 | .51130 | .51347 | .51565 |
| II 10 | .0090000 | .49750 | .49993 | .50219 | .50437 | .50645 | .50847 |

| Solution number | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| | E | E | E | E | E | E | E |
| II 1 | 0.59608 | 0.59897 | 0.60196 | 0.60405 | 0.60739 | 0.61004 | 0.61278 |
| II 2 | .57515 | .57770 | .58047 | .58284 | .58530 | .58775 | .59005 |
| II 3 | .57362 | .57628 | .57871 | .58133 | .58375 | .58619 | .58853 |
| II 4 | .55590 | .55832 | .56070 | .56285 | .56499 | .56715 | .56900 |
| II 5 | .55418 | .55658 | .55896 | .56105 | .56323 | .56538 | .56739 |
| II 6 | .54596 | .54829 | .55053 | .55258 | .55451 | .55654 | .55841 |
| II 7 | .54006 | .54225 | .54449 | .54639 | .54833 | .55025 | .55206 |
| II 8 | .52962 | .53180 | .53365 | .53545 | .53718 | .53906 | .54082 |
| II 9 | .51768 | .51959 | .52139 | .52302 | .52462 | .52627 | .52783 |
| II 10 | .51044 | .51237 | .51394 | .51539 | .51699 | .51852 | .51990 |

TABLE 3.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES III. MOLALITY OF o-PHTHALIC ACID = MOLALITY OF ACID POTASSIUM PHTHALATE = 0.018

| Solution number | Molality of KCl | Temperature in degrees centigrade | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 |
| | *Moles of solute per 1,000 g of water* | E | E | E | E | E | E |
| III 1 | 0.005 | 0.52279 | 0.52569 | 0.52850 | 0.53116 | 0.53375 | 0.53630 |
| III 2 | .0079994 | .51179 | .51446 | .51708 | .51954 | .52193 | .52433 |
| III 3 | .010 | .50655 | .50917 | .51166 | .51402 | .51632 | .51856 |
| III 4 | .014 | .49867 | .50109 | .50352 | .50573 | .50788 | .51005 |
| III 5 | .018 | .49282 | .49516 | .49744 | .49951 | .50154 | .50354 |

| Solution number | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| | E | E | E | E | E | E | E |
| III 1 | 0.53873 | 0.54098 | 0.54327 | 0.54534 | 0.54739 | 0.54957 | 0.55153 |
| III 2 | .52649 | .52859 | .53064 | .53249 | .53441 | .53629 | .53812 |
| III 3 | .52070 | .52264 | .52465 | .52638 | .52823 | .53002 | .53184 |
| III 4 | .51197 | .51380 | .51563 | .51718 | .51898 | .52059 | .52215 |
| III 5 | .50541 | .50717 | .50891 | .51039 | .51196 | .51360 | .51496 |

TABLE 4.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES IV. {MOLALITY OF o-PHTHALIC ACID=0.015. MOLALITY OF ACID POTASSIUM PHTHALATE=0.000.

| Solution number | Molality of KCl | Temperature in degrees centigrade | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 |
| | *Moles of solute per 1,000 g of water* | *v* | *v* | *v* | *v* | *v* | *v* |
| IV 1 | 0.003 | 0.52310 | 0.52607 | 0.52877 | 0.53135 | 0.53394 | 0.53647 |
| IV 2 | .005 | .51119 | .51385 | .51639 | .51876 | .52117 | .52337 |
| IV 3 | .006985 | .50340 | .50589 | .50833 | .51155 | .51280 | .51491 |
| IV 4 | .009 | .49749 | .49987 | .50223 | .50433 | .50642 | .50846 |
| IV 5 | .049305 | .45838 | .46008 | .46170 | .46315 | .46455 | .46582 |

| Solution number | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| | *v* | *v* | *v* | *v* | *v* | *v* | *v* |
| IV 1 | 0.53884 | 0.54110 | 0.54323 | 0.54526 | 0.54727 | 0.54939 | 0.55127 |
| IV 2 | .52558 | .52713 | .52960 | .53133 | .53317 | .53500 | .53664 |
| IV 3 | .51693 | .51885 | .52066 | .52226 | .52394 | .52564 | .52718 |
| IV 4 | .51037 | .51218 | .51391 | .51538 | .51697 | .51852 | .52000 |
| IV 5 | .46702 | .46800 | .46907 | .46985 | .47006 | .47146 | .47217 |

TABLE 5.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides.*

SERIES V. {MOLALITY OF o-PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE.

| Solution number | Molality of KHPh | Temperature in degrees centigrade | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 15 | 20 | 25 |
| | *Moles of solute per 1,000 g of water* | *v* | *v* | *v* | *v* | *v* | *v* |
| V 1 | 0.0009423 | 0.56610 | 0.56970 | 0.57319 | 0.57648 | 0.57974 | 0.58276 |
| V 2 | .0016280 | .54703 | .55030 | .55343 | .55641 | .55938 | .56215 |
| V 3 | .0026071 | .53145 | .53440 | .53726 | .54009 | .54269 | .54537 |
| V 4 | .0030788 | .52614 | .52906 | .53188 | .53453 | .53704 | .53957 |
| V 5 | .0036444 | .52077 | .52358 | .52631 | .52887 | .53143 | .53371 |
| V 6 | .0038552 | .51909 | .52185 | .52456 | .52710 | .52947 | .53182 |
| V 7 | .0041264 | .51697 | .51973 | .52237 | .52486 | .52730 | .52956 |
| V 8 | .0044082 | .51489 | .51757 | .52021 | .52271 | .52503 | .52741 |
| V 9 | .0054960 | .50820 | .51091 | .51342 | .51573 | .51795 | .52023 |
| V 10 | .0056467 | .50740 | .51010 | .51255 | .51486 | .51711 | .51931 |

| Solution number | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| | *v* | *v* | *v* | *v* | *v* | *v* | *v* |
| V 1 | 0.59198 | 0.59486 | 0.59157 | 0.59408 | 0.59665 | 0.59924 | 0.60162 |
| V 2 | .56488 | .56751 | .56998 | .57210 | .57450 | .57680 | .57894 |
| V 3 | .54777 | .55002 | .55228 | .55437 | .55618 | .55846 | .56037 |
| V 4 | .54158 | .54417 | .54626 | .54826 | .55015 | .55220 | .55412 |
| V 5 | .53604 | .53829 | .54033 | .54216 | .54407 | .54603 | .54776 |
| V 6 | .53419 | .53629 | .53829 | .54015 | .54196 | .54389 | .54558 |
| V 7 | .53185 | .53392 | .53592 | .53774 | .53958 | .54142 | .54314 |
| V 8 | .52955 | .53164 | .53364 | .53544 | .53717 | .53903 | .54071 |
| V 9 | .52229 | .52423 | .52616 | .52777 | .52954 | .53127 | .53284 |
| V 10 | .52134 | .52322 | .52516 | .52676 | .52849 | .53027 | .53183 |

The hydrogen-ion concentration for each solution was calculated by eq 12 and by the use of the data for $E°$ determined by Harned and Ehlers [12], the values of $R$, $T$, and $F$ given by Hamer, Burton, and Acree [13], and (1) the limiting law of Debye and Hückel; (2) the Guggenheim expression; (3) the extended equation of Debye and Hückel, in which $a_i$ was taken equal to 3.76 A for each temperature; and (4) the Hückel extension of the Debye-Hückel equation in which $a_i$ was taken equal to 3.76 A and the $\beta$ term was calculated from the values of $\beta$ of the various ions given in another paper [1]. Method (4) is subsequently designated as the complete method. The value of 3.76 A for $a_i$ was reported in another paper [1] on the determination of the second dissociation constant of *o*-phthalic acid. It is to be expected that the same value of $a_i$ should apply to the complete system of *o*-phthalic acid and potassium hydroxide regardless of the pH values. For example, Harned, Morrison, Walker, Donelson, and Calmon [14] found that the value of $a_i$ for hydrochloric acid at 25° C did not change significantly in going from pure water with dielectric constant of 78.54 to a 82-percent dioxane-water mixture of dielectric constant of 10. As the dielectric constants of solutions suitable for the determination of $K_1$ and $K_2$ for *o*-phthalic acid should be nearly the same, it is to be expected that the same $a_i$ value should apply. The values of $\beta_{Cl}$, $\beta_{HPh}$, and $\beta_{Ph}$ for use with the respective concentrations of the ions were taken from another paper on the determination of the second dissociation constant of *o*-phthalic acid, and $\beta_H$ is taken equal to $\beta_{Cl}$[5].

The four different sets of $m_H$ values were then used in eqs. 10 and 11 to calculate values of $m_{H_2Ph}$ and $m_{HPh}$, which were used in eq 17 to calculate values of $pK'_1$. In this calculation $m_{Ph}$ was taken equal to zero. Values of $pK'_1$ calculated in this manner for a temperature of 25° C are given in table 6 in the columns labeled "without overlapping corrections".

TABLE 6.—*Summary of* $pK'_1$ *values at 25° C for o-phthalic acid obtained by different methods of calculation*

SERIES I. {MOLALITY OF o-PHTHALIC ACID = 1.5 × MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE = MOLALITY OF ACID POTASSIUM PHTHALATE.

| Molality of acid potassium phthalate | $pK'_1$ (without overlapping corrections)[a] | | | | $pK'_1$ (with overlapping corrections)[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | Limiting law of Debye and Hückel | Guggenheim | 3.76 A | 3.76 A and $\beta$ | Limiting law of Debye and Hückel | Guggenheim | 3.76 A | 3.76 A and $\beta$ |
| 0.0018357 | 2.9369 | 2.9405 | 2.9412 | 2.9417 | 2.9477 | 2.9487 | 2.9494 | 2.9496 |
| .0019071 | 2.9365 | 2.9402 | 2.9409 | 2.9414 | 2.9482 | 2.9493 | 2.9490 | 2.9492 |
| .0027658 | 2.9376 | 2.9417 | 2.9426 | 2.9432 | 2.9471 | 2.9477 | 2.9495 | 2.9498 |
| .0034165 | 2.9384 | 2.9427 | 2.9434 | 2.9440 | 2.9472 | 2.9492 | 2.9501 | 2.9504 |
| .0039521 | 2.9378 | 2.9422 | 2.9430 | 2.9436 | 2.9482 | 2.9485 | 2.9494 | 2.9497 |
| .0040518 | 2.9368 | 2.9391 | 2.9409 | 2.9435 | 2.9481 | 2.9484 | 2.9493 | 2.9496 |
| .0046056 | 2.9372 | 2.9418 | 2.9426 | 2.9432 | 2.9484 | 2.9489 | 2.9488 | 2.9492 |
| .0047953 | 2.9389 | 2.9436 | 2.9440 | 2.9450 | 2.9470 | 2.9495 | 2.9504 | 2.9508 |
| .0068606 | 2.9377 | 2.9428 | 2.9436 | 2.9443 | 2.9452 | 2.9482 | 2.9493 | 2.9497 |
| .0079547 | 2.9380 | 2.9433 | 2.9442 | 2.9449 | 2.9433 | 2.9485 | 2.9496 | 2.9500 |
| .0081020 | 2.9372 | 2.9425 | 2.9433 | 2.9441 | 2.9445 | 2.9477 | 2.9488 | 2.9492 |
| .011058 | 2.9369 | 2.9427 | 2.9439 | 2.9447 | 2.9430 | 2.9476 | 2.9487 | 2.9496 |
| .011799 | 2.9366 | 2.9424 | 2.9433 | 2.9441 | 2.9439 | 2.9477 | 2.9488 | 2.9491 |
| .011913 | 2.9360 | 2.9418 | 2.9427 | 2.9435 | 2.9432 | 2.9467 | 2.9478 | 2.9483 |
| .012000 | 2.9373 | 2.9431 | 2.9440 | 2.9448 | 2.9446 | 2.9482 | 2.9493 | 2.9498 |

See footnotes at end of table.

[5] It is well known that the activity coefficient of an ion cannot be determined experimentally without some assumption. In this paper the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. For more details regarding assumptions in pH determinations, see references [9, 13, 15, and 16].

TABLE 6.—*Summary of $pK'_1$ values at 25° C for o-phthalic acid obtained by different methods of calculation*—Continued

SERIES II. {MOLALITY OF o-PHTHALIC ACID=2×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.

| Molality of acid potassium phthalate | $pK'_1$ (without overlapping corrections)[a] | | | | $pK'_1$ (with overlapping corrections)[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | Limiting law of Debye and Hückel | Guggenheim | 3.76 A | 3.76 A and $\beta$ | Limiting law of Debye and Hückel | Guggenheim | 3.76 A | 3.76 A and $\beta$ |
| 0.00081865 | 2.9343 | 2.9377 | 2.9383 | 2.9388 | 2.9483 | 2.9486 | 2.9491 | 2.9493 |
| .0014005 | 2.9371 | 2.9409 | 2.9417 | 2.9422 | 2.9474 | 2.9486 | 2.9493 | 2.9495 |
| .0014548 | 2.9376 | 2.9412 | 2.9420 | 2.9425 | 2.9475 | 2.9487 | 2.9495 | 2.9497 |
| .0023517 | 2.9390 | 2.9430 | 2.9438 | 2.9445 | 2.9482 | 2.9502 | 2.9500 | 2.9500 |
| .0024641 | 2.9395 | 2.9436 | 2.9445 | 2.9451 | 2.9473 | 2.9494 | 2.9502 | 2.9507 |
| .0031025 | 2.9381 | 2.9430 | 2.9437 | 2.9443 | 2.9455 | 2.9479 | 2.9489 | 2.9483 |
| .0036743 | 2.9393 | 2.9440 | 2.9451 | 2.9457 | 2.9482 | 2.9499 | 2.9499 | 2.9513 |
| .0050000 | 2.9394 | 2.9446 | 2.9457 | 2.9465 | 2.9459 | 2.9490 | 2.9501 | 2.9507 |
| .0071782 | 2.9381 | 2.9449 | 2.9450 | 2.9459 | 2.9443 | 2.9480 | 2.9493 | 2.9499 |
| .0090000 | 2.9375 | 2.9436 | 2.9449 | 2.9458 | 2.9435 | 2.9475 | 2.9487 | 2.9493 |

SERIES III. MOLALITY OF o-PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTALATE=0.018

| *Molality of potassium chloride* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| .005 | 2.9384 | 2.9417 | 2.9424 | 2.9427 | 2.9459 | 2.9490 | 2.9497 | 2.9500 |
| .008 | 2.9377 | 2.9425 | 2.9435 | 2.9438 | 2.9456 | 2.9490 | 2.9496 | 2.9498 |
| .010 | 2.9376 | 2.9423 | 2.9434 | 2.9436 | 2.9452 | 2.9489 | 2.9495 | 2.9500 |
| .014 | 2.9372 | 2.9413 | 2.9421 | 2.9425 | 2.9433 | 2.9480 | 2.9487 | 2.9494 |
| .018 | 2.9351 | 2.9404 | 2.9414 | 2.9421 | 2.9429 | 2.9481 | 2.9490 | 2.9494 |

SERIES IV. {MOLALITY OF o-PHTHALIC ACID=0.018 MOLALITY OF ACID POTASSIUM PHTHALATE=0.009

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.0030 | 2.9406 | 2.9448 | 2.9457 | 2.9461 | 2.9463 | 2.9484 | 2.9491 | 2.9494 |
| .0050 | 2.9384 | 2.9432 | 2.9441 | 2.9447 | 2.9440 | 2.9468 | 2.9476 | 2.9481 |
| .0070 | 2.9382 | 2.9439 | 2.9450 | 2.9458 | 2.9440 | 2.9474 | 2.9483 | 2.9490 |
| .0090 | 2.9361 | 2.9434 | 2.9446 | 2.9455 | 2.9430 | 2.9470 | 2.9482 | 2.9488 |
| .0493 | 2.9210 | 2.9409 | 2.9443 | 2.9485 | 2.9278 | 2.9456 | 2.9490 | 2.9497 |

SERIES V. {MOLALITY OF o-PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE.

| *Molality of acid potassium phthalate* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.0009423 | 2.9406 | 2.9330 | 2.9340 | 2.9345 | 2.9468 | 2.9476 | 2.9482 | 2.9481 |
| .0016280 | 2.9314 | 2.9367 | 2.9377 | 2.9383 | 2.9473 | 2.9489 | 2.9497 | 2.9491 |
| .0026071 | 2.9360 | 2.9412 | 2.9422 | 2.9430 | 2.9463 | 2.9488 | 2.9498 | 2.9498 |
| .0030788 | 2.9374 | 2.9427 | 2.9437 | 2.9445 | 2.9466 | 2.9494 | 2.9505 | 2.9507 |
| .0036444 | 2.9346 | 2.9399 | 2.9411 | 2.9419 | 2.9450 | 2.9481 | 2.9492 | 2.9491 |
| .0038552 | 2.9342 | 2.9396 | 2.9408 | 2.9417 | 2.9442 | 2.9473 | 2.9485 | 2.9481 |
| .0041264 | 2.9354 | 2.9337 | 2.9420 | 2.9429 | 2.9451 | 2.9486 | 2.9491 | 2.9498 |
| .0044082 | 2.9362 | 2.9417 | 2.9429 | 2.9438 | 2.9439 | 2.9484 | 2.9495 | 2.9493 |
| .0054960 | 2.9368 | 2.9421 | 2.9440 | 2.9450 | 2.9438 | 2.9476 | 2.9488 | 2.9488 |
| .0056467 | 2.9367 | 2.9427 | 2.9439 | 2.9450 | 2.9439 | 2.9477 | 2.9489 | 2.9490 |

[a] The different values of $pK'_1$ do not converge to a single value in the limit of infinite dilution or zero ionic strength.

[b] The different values of $pK'_1$ do not converge to a single value in the limit of infinite dilution or zero ionic strength. The limiting values of $pK_1$ at infinite dilution obtained by the "limiting-law" of Debye and Hückel and with the use of $a_i$=3.76 A and $\beta$ values differ by 0.0006; this difference being real. The value of $pK_1$ obtained with the use of $a_i$ and $\beta$ is accepted as the better value.

The values of $pK'_1$ calculated by the various methods are quite different. In figure 1 the "limiting-law" values (curve *A*) and the

"complete" values (curve *B*) are shown plotted as functions of the ionic strength for 25° C. In the range of low concentration the plots exhibit a marked curvature which arises from the neglect of "overlapping corrections." If this curvature is ignored, a straight line through the other points gives $pK_1=2.9388$ by the limiting law and $pK_1=2.9471$ by the complete treatment on extrapolation to infinite dilution or zero ionic strength. These values correspond, respectively, to values of 0.001151 and 0.001130 for $K_1$, which differ by

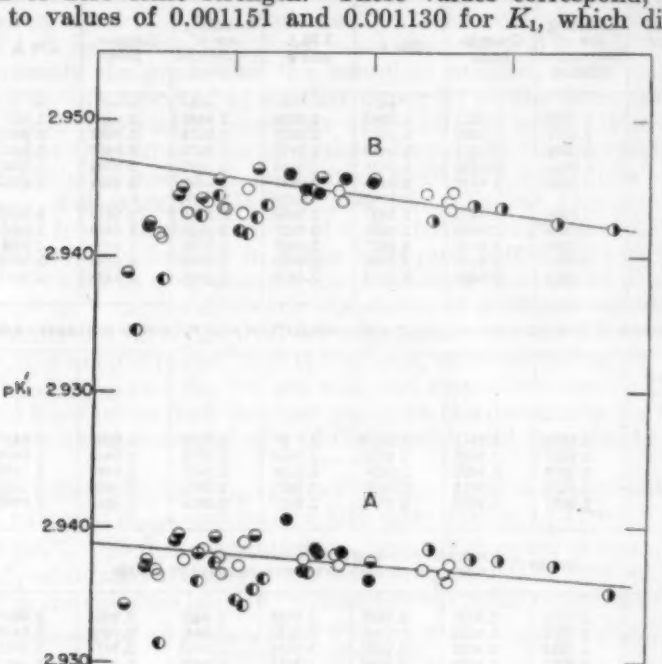


FIGURE 1.—*Plots of the values of* $pK_1$ *as a function of the ionic strength of the solutions at 25° C without corrections for the amounts of phthalate ion in the solutions.*

*A*, Values obtained by using the limiting law of Debye and Hückel for the ionic activity coefficients; *B*, values obtained by using the Hückel extension of the Debye-Hückel equation for the ionic activity coefficients in which $a_i=3.76$ A, $\beta_H=-0.10$, $\beta_{Cl}=-0.10$, $\beta_{HPh}=-0.023$, and $\beta_{Ph}=-0.38$.

○=Series I. ●=Series IV.
◒=Series II. ◐=Series V.
◑=Series III.

approximately 2 percent. In other words, the values of $pK'_1$ calculated by the limiting law and by the complete treatment do not converge to the same value when they are plotted against the ionic strength.

These values of $K_1$ and the same data for $m_H$ previously used are then employed in eq 15 to calculate values of $m_{Ph}$, which are then inserted in eq 10 and 11 to obtain new values of $m_{H_2Ph}$ and $m_{HPh}$. These in turn are used in eq 17 to calculate values of $pK'_1$. The "limiting-law" and "complete" values are shown plotted in part I of figure 2 as functions of the ionic strength at 25° C.

The curvatures of figure 1 have been eliminated by the corrections for $m_{Ph}$. Extrapolations to infinite dilution can then be made with certainty. The "limiting-law" values give $pK_1=2.9469$ and the "complete" values give $pK_1=2.9491$, which correspond, respectively, to 0.001130 and 0.001124 for $K_1$, which differ by approximately 0.6 percent. Again, convergence has not been obtained. However, the assigned ionic strength and $m_H$ of the solutions are altered by taking into account the presence of the diphthalate ion.

Repeating all the above processes with the new ionic strength gives new values of $pK'_1$, which are given in table 6 for a temperature of 25° C in the columns labeled "with overlapping" corrections. In figure 2,

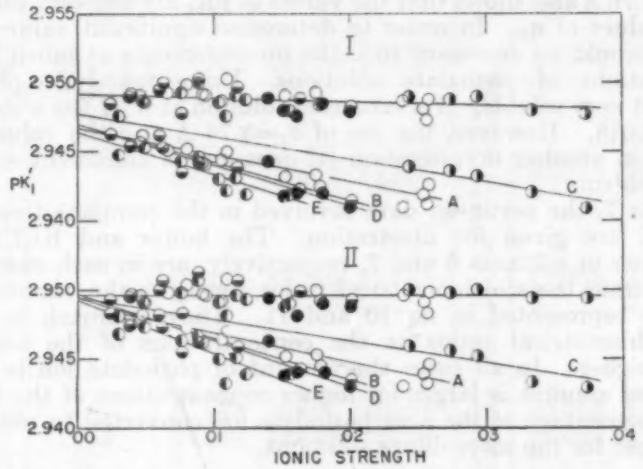


FIGURE 2.—*Plots of the values of* $pK_1$ *for 25° C with corrections for the amounts of phthalate ion present in the solutions as a function of the ionic strength of the solutions.*

Part I, Data based upon values of the hydrogen-ion concentration calculated without corrections for the amount of phthalate ion; part II, data based upon values of the hydrogen-ion concentration calculated with corrections for the amount of phthalate ion; upper curves, values obtained by using the Hückel extension of the Debye-Hückel equation for the ionic activity coefficients in which $a_i=3.76$ A, $\beta_H=-0.10$, $\beta_{Cl}=-0.10$, $\beta_{HPh}=-0.023$, and $\beta_{Ph}=-0.38$; lower curves, values obtained by using the limiting law of Debye and Hückel for the ionic activity coefficients.

○=Series I (*A*) ●=Series IV (*D*)
◒=Series II (*B*) ◐=Series V (*E*)
◑=Series III (*C*)

part II, the final or complete values of $pK'_1$, are shown plotted with respect to the ionic strength. Extrapolation to zero ionic strength gives $pK_1=2.9490$ (on the average) by the limiting law and $pK_1=2.9496$ by the complete method. These values correspond, respectively, to 0.001125 and 0.001123 for $K_1$. Exact convergence of the $pK'_1$ again has not been obtained. However, as $a_i$ was shown to have a value of 3.76 A in a previous paper [1], it is believed that values of $pK$ obtained with its use are the correct values.[6]

[6] Lack of convergence of $pK'$ values calculated by the limiting law or with the use of some $a_i$ value is not restricted to the present case. The data obtained by Nims [27] for the first dissociation constant of phosphoric acid and by Hamer [3] for the bisulfate ion likewise show lack of convergence to a single thermodynamic value of the dissociation constant when the limiting law or some value of $a_i$ is used. The lack of convergence is greater for the bisulfate ion than for phosphoric acid because its dissociation constant has a higher value. The lack of convergence arises from the fact that extrapolation must be made with data for different buffer ratios caused by the corrections for hydrogen-ion concentration. As values of $a_i$ are not known for the first dissociation of phosphoric acid and sulfuric acid there is some uncertainty about the values of the dissociation constants of these acids. This uncertainty about the value of $a_i$ to use is believed to be eliminated in the present case.

The values of $pK'_1$ calculated by the limiting law are dependent upon the ionic strength whereas those calculated by the complete method are not. The complete treatment is quite insensitive to the values of $\beta$, however, and hence gives only a qualitative confirmation of the accuracy of the $\beta$ values determined in the investigation of the second dissociation constant of *o*-phthalic acid. Comparison of the values of $pK_1$ given in the last 2 columns of table 6 show that the values of $pK_1$ calculated with or without the use of the $\beta$ values are not appreciably different.

Comparison of the data of column 7 obtained with an $a_i$ value of 3.00 A (Guggenheim values) and of column 8 obtained with an $a_i$ value of 3.76 A also shows that the values of $pK_1$ are not very sensitive to the values of $a_i$. In order to determine significant values of $a_i$ and $\beta$ it would be necessary to make measurements at much higher concentrations of phthalate solutions. Unfortunately, *o*-phthalic acid is not very soluble. Its saturated solution at 0° C has a molality of only 0.018. However, the use of $a_i=3.76$ A and the values of $\beta$ obtained in another investigation [1] does give a consistent solution of the problem.

In table 7, the pertinent data involved in the complete treatment at 25° C are given for illustration. The buffer and KCl/KHPh ratios given in columns 6 and 7, respectively, are in each case quite different from the stoichiometrical ratios, owing to the various ionic equilibria represented in eq 10 and 11. They approach in value the stoichiometrical ratios as the concentrations of the solutions become higher. In all cases the amount of phthalate ion is small. The actual amount is larger for higher concentrations of the buffer, but the percentage of the acid phthalate ion converted to phthalate ion is larger for the more dilute solutions.

TABLE 7.—*Summary of the values of the concentrations of the ionic and molecular species of phthalate-chloride mixtures and of the first dissocia-*

TABLE 7.—*Summary of the values of the concentrations of the ionic and molecular species of phthalate-chloride mixtures and of the first dissociation constant of o-phthalic acid at 25° C*

SERIES I. {MOLALITY OF o-PHTHALIC ACID=1.5 × MOLALITY OF ACID POTASSIUM PHTHALATE. / MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.

| Molality of acid potassium phthalate | Molality of undissociated o-phthalic acid | Molality of acid phthalate ion | Molality of phthalate ion | Molality of hydrogen ion | $\frac{H_2Ph}{HPh}$ | $\frac{KCl}{HPh}$ | $K'_1 \times 10^3$ (without corrections for activity coefficients) | $K'_1 \times 10^3$ (with Debye-Hückel limiting law corrections) | $K'_1 \times 10^3$ (with corrections for activity coefficients when $a_i$=3.76 A) | $K'_1 \times 10^3$ (with total corrections for activity coefficients) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0018357 | 0.0018696 | 0.0027052 | 0.000015 | 0.00089854 | 0.6911 | 0.6786 | 1.3001 | 1.1090 | 1.1228 | 1.1231 |
| .0019071 | .0019604 | .0027918 | .000016 | .00091588 | .7022 | .6831 | 1.3043 | 1.1095 | 1.1237 | 1.1241 |
| .0027658 | .0030859 | .0038103 | .000017 | .0010810 | .8099 | .7259 | 1.3348 | 1.1027 | 1.1219 | 1.1225 |
| .0034165 | .0039653 | .0045572 | .000019 | .0011782 | .8701 | .7497 | 1.3540 | 1.0970 | 1.1200 | 1.1210 |
| .0039521 | .0047005 | .0051569 | .000023 | .0012506 | .9115 | .7664 | 1.3720 | 1.0956 | 1.1222 | 1.1228 |
| .0040518 | .0048653 | .0052539 | .000026 | .0012738 | .9260 | .7712 | 1.3755 | 1.0952 | 1.1223 | 1.1231 |
| .0046056 | .0056086 | .0058772 | .000028 | .0013279 | .9543 | .7836 | 1.3915 | 1.0931 | 1.1234 | 1.1241 |
| .0047953 | .0058731 | .0060946 | .000031 | .0013406 | .9637 | .7868 | 1.3912 | 1.0881 | 1.1194 | 1.1200 |
| .0068606 | .0087979 | .0083211 | .000032 | .0015255 | 1.0373 | .8245 | 1.4428 | 1.0793 | 1.1219 | 1.1228 |
| .0079547 | .010369 | .0094885 | .000033 | .0016001 | 1.0927 | .8383 | 1.4643 | 1.0779 | 1.1211 | 1.1220 |
| .0081020 | .010574 | .0096357 | .000040 | .0016131 | 1.0974 | .8408 | 1.4699 | 1.0780 | 1.1231 | 1.1241 |
| .011058 | .014924 | .012741 | .000050 | .0017820 | 1.1713 | .8679 | 1.5217 | 1.0582 | 1.1218 | 1.1231 |
| .011799 | .016007 | .013512 | .000053 | .0018189 | 1.1847 | .8732 | 1.5354 | 1.0557 | 1.1229 | 1.1243 |
| .011913 | .016175 | .013622 | .000060 | .0018290 | 1.1874 | .8745 | 1.5403 | 1.0570 | 1.1252 | 1.1264 |
| .012000 | .016229 | .013724 | .000047 | .0018165 | 1.1825 | .8744 | 1.5361 | 1.0528 | 1.1211 | 1.1225 |

SERIES II. {MOLALITY OF o-PHTHALIC ACID=2×MOLALITY OF ACID POTASSIUM PHTHALATE. / MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.00081865 | 0.00090865 | 0.0015352 | 0.000012 | 0.00074083 | 0.5919 | 0.5333 | 1.2517 | 1.1159 | 1.1232 | 1.1238 |
| .0014005 | .0018234 | .0023656 | .000012 | .00099005 | .7708 | .5920 | 1.2845 | 1.1119 | 1.1229 | 1.1233 |
| .0014548 | .0019128 | .0024392 | .000012 | .0010090 | .7842 | .5964 | 1.2867 | 1.1107 | 1.1225 | 1.1228 |
| .0023517 | .0034476 | .0035933 | .000014 | .0012700 | .9595 | .6545 | 1.3237 | 1.1039 | 1.1216 | 1.1220 |
| .0024641 | .0036463 | .0037332 | .000015 | .0012947 | .9767 | .6601 | 1.3256 | 1.1014 | 1.1196 | 1.1202 |
| .0031025 | .0047844 | .0045043 | .000017 | .0014393 | 1.0622 | .6888 | 1.3550 | 1.1034 | 1.1258 | 1.1264 |
| .0036743 | .0058295 | .0051775 | .000018 | .0015350 | 1.1259 | .7097 | 1.3633 | 1.0923 | 1.1181 | 1.1187 |
| .0050000 | .0082841 | .0066995 | .000019 | .0017324 | 1.2365 | .7463 | 1.4010 | 1.0862 | 1.1195 | 1.1202 |
| .0071782 | .012403 | .0091054 | .000026 | .0019795 | 1.3622 | .7883 | 1.4532 | 1.0763 | 1.1215 | 1.1223 |
| .0090000 | .015896 | .011068 | .000036 | .0021404 | 1.4362 | .8132 | 1.4904 | 1.0677 | 1.1224 | 1.1238 |

See footnote at end of table.

TABLE 7.—*Summary of the values of the concentrations of the ionic and molecular species of phthalate-chloride mixtures and of the first dissociation constant of o-phthalic acid at 25° C*—Continued

SERIES III. MOLALITY OF o-PHTHALIC ACID = MOLALITY OF ACID POTASSIUM PHTHALATE = 0.018.

| Molality of potassium chloride | Molality of undissociated o-phthalic acid | Molality of acid phthalate ion | Molality of phthalate ion | Molality of hydrogen ion | $\frac{H_2Ph}{HPh}$ | $\frac{KCl}{HPh}$ | $K'_1 \times 10^3$ (without corrections for activity coefficients) | $K'_1 \times 10^3$ (with Debye-Hückel limiting law corrections) | $K'_1 \times 10^3$ (with corrections for activity coefficients when $a_i$=3.76 A) | $K'_1 \times 10^3$ (with total corrections for activity coefficients) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.005 | 0.016765 | 0.019135 | 0.000100 | 0.0013352 | 0.8761 | 0.2613 | 1.5239 | 1.0559 | 1.1205 | 1.1221 |
| .008 | .016733 | .019185 | .000082 | .0013497 | .8722 | .4170 | 1.5478 | 1.0492 | 1.1212 | 1.1225 |
| .010 | .016734 | .019169 | .000097 | .0013639 | .8730 | .5217 | 1.5623 | 1.0441 | 1.1205 | 1.1221 |
| .014 | .016694 | .019236 | .000071 | .0013819 | .8678 | .7278 | 1.5924 | 1.0332 | 1.1199 | 1.1236 |
| .018 | .016689 | .019214 | .000096 | .0014062 | .8686 | .9368 | 1.6190 | 1.0276 | 1.1221 | 1.1238 |

SERIES IV. {MOLALITY OF o-PHTHALIC ACID = 0.018. MOLALITY OF ACID POTASSIUM PHTHALATE = 0.000.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0030 | 0.015960 | 0.011005 | 0.000035 | 0.0020756 | 1.4502 | 0.2726 | 1.4312 | 1.0830 | 1.1225 | 1.1236 |
| .0050 | .015038 | .011013 | .000049 | .0021096 | 1.4472 | .4540 | 1.4577 | 1.0816 | 1.1265 | 1.1269 |
| .0070 | .015912 | .011052 | .000036 | .0021206 | 1.4397 | .6334 | 1.4729 | 1.0735 | 1.1233 | 1.1246 |
| .0090 | .015895 | .011067 | .000037 | .0021431 | 1.4363 | .8132 | 1.4921 | 1.0689 | 1.1237 | 1.1251 |
| .0493 | .015601 | .011412 | .000005 | .0023879 | 1.3671 | 4.3200 | 1.7467 | 0.9789 | 1.1210 | 1.1228 |

SERIES V. {MOLALITY OF o-PHTHALIC ACID = 1.5 × MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE = 1.5 × MOLALITY OF ACID POTASSIUM PHTHALATE.

| *Molality of acid potassium phthalate* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0009423 | 0.00078617 | 0.0015553 | 0.000014 | 0.00064143 | 0.5055 | 0.9068 | 1.2690 | 1.1156 | 1.1249 | 1.1251 |
| .0016280 | .0016036 | .0024479 | .000015 | .00085693 | .6551 | .9976 | 1.3081 | 1.1091 | 1.1238 | 1.1243 |
| .0026071 | .0028631 | .0036406 | .000016 | .0010614 | .7864 | 1.0742 | 1.3497 | 1.1001 | 1.1221 | 1.1225 |
| .0030788 | .0034930 | .0041919 | .000018 | .0011372 | .8333 | 1.1017 | 1.3647 | 1.0944 | 1.1197 | 1.1202 |
| .0036444 | .0042636 | .0048186 | .000020 | .0012306 | .8848 | 1.1345 | 1.3908 | 1.0950 | 1.1248 | 1.1243 |
| .0038552 | .0045389 | .0050506 | .000024 | .0012521 | .9026 | 1.1450 | 1.3872 | 1.0855 | 1.1164 | 1.1170 |
| .0041264 | .0049275 | .0053610 | .000025 | .0012897 | .9191 | 1.1546 | 1.4032 | 1.0894 | 1.1222 | 1.1231 |
| .0044082 | .0053180 | .0056764 | .000025 | .0013224 | .9369 | 1.1649 | 1.4115 | 1.0871 | 1.1221 | 1.1238 |
| .0054960 | .0068326 | .0068883 | .000025 | .0014336 | .9919 | 1.1968 | 1.4453 | 1.0821 | 1.1241 | 1.1251 |
| .0056467 | .0070466 | .0070449 | .000026 | .0014487 | 1.0002 | 1.2023 | 1.4484 | 1.0805 | 1.1237 | 1.1246 |

* Molality of o-phthalic acid = 1.5063 × molality of acid potassium phthalate and molality of potassium chloride = molality of acid potassium phthalate.

From the results of series III and IV, it was found that additions of potassium chloride to a solution of the same buffer ratio lowers the pH value of the solutions, causes a decrease in the amounts of undissociated *o*-phthalic acid and phthalate ion, and produces increases in the amounts of acid phthalate and hydrogen ions. In other words the tendency of reaction 7 to proceed from left to right is decreased by the addition of potassium chloride. In figure 3, the values of $pK'_1$ with and without corrections for activity coefficients are shown plotted as functions of the ionic strength for 25° C. All the data

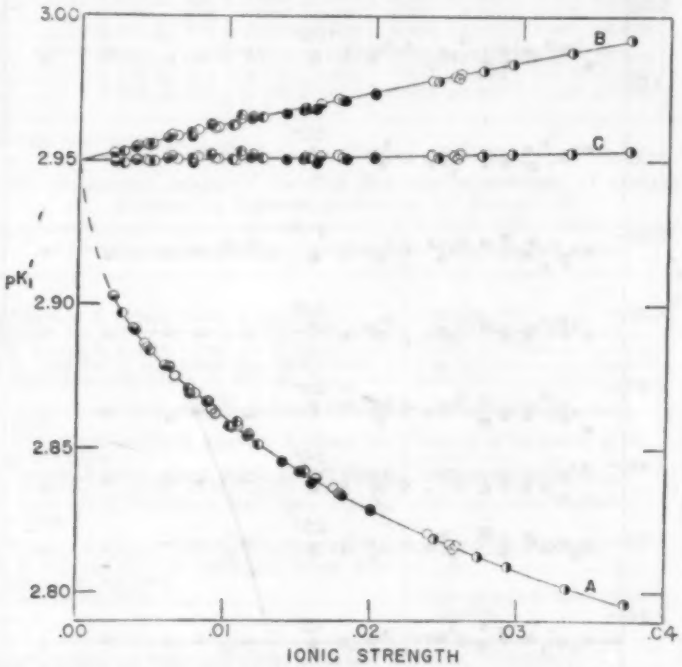


FIGURE 3.—*Plots of the values of* $pK'_1$ *for 25° C as a function of the ionic strength of the solution.*

In each case, the same values of the ionic and molecular species were employed.

*A*, Without corrections for activity coefficients; *B*, with corrections for activity coefficients based upon the limiting law of Debye and Hückel; *C*, with corrections for the activity coefficients based upon the Debye-Hückel equation in which $a_i$=3.76 A.

The values for the various series of experiments fall on the same curves for the scale used in the construction of the graph.

extrapolate to the same limiting value for $pK_1$. These curves are based upon the same values of the ionic and molecular species (calculated by the complete method) whereas the data plotted in figures 1 and 2 were for different values of the ionic and molecular species. For this reason convergence of the values of $pK'_1$ to a single thermodynamic value at infinite dilution is obtained.

In figure 4 the values obtained by the complete method are shown plotted as functions of the ionic strength at several other temperatures. The average values of $pK_1$ with the mean deviation for series I, II, and V are given in table 8. The average of the three determinations and the total mean deviation is given in column 5 for each tem-

perature. The deviations range from 0.0005 to 0.0011, which correspond to 0.03–0.07 mv in the emf. Values of the first dissociation constant of *o*-phthalic acid are given in the last column of the table.

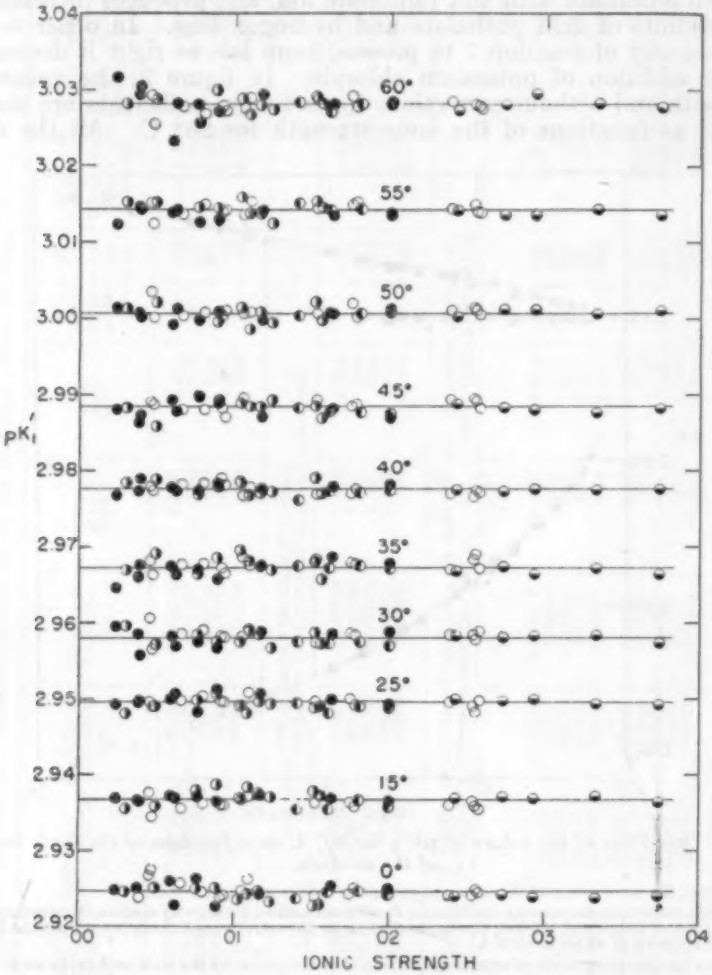


FIGURE 4.—*Plots of the values of* $pK'_1$ *calculated by the complete method for several temperatures as a function of the ionic strength of the solutions.*

○=Series I. ●=Series IV.
◒=Series II. ◐=Series V.
◑=Series III.

In table 9 the values of $K_1$ are compared with those obtained by other investigators at 18° and 25° C. A critical comparison is not possible as previous investigations were restricted to a single temperature and involved a number of uncertainties.

TABLE 8.—*Summary of numerical values of* $pK_1$ *and* $K_1$ *calculated from measurements of three different buffer ratios at temperatures of 0° to 60° C*

| Temperature | $pK_1$ | | | | $K_1 \times 10^3$ |
|---|---|---|---|---|---|
| *t°C* | Series I | Series II | Series V | Average | |
| 0 | [a] 2.9250 ±0.0009 | 2.9246 ±0.0014 | 2.9241 ±0.0007 | 2.9246 ±0.0010 | 1.190 |
| 5 | 2.9273 ±0.0006 | 2.9269 ±0.0008 | 2.9276 ±0.0010 | 2.9273 ±0.0008 | 1.182 |
| 10 | 2.9316 ±0.0005 | 2.9308 ±0.0008 | 2.9319 ±0.0009 | 2.9314 ±0.0008 | 1.171 |
| 15 | 2.9361 ±0.0005 | 2.9368 ±0.0006 | 2.9373 ±0.0007 | 2.9367 ±0.0006 | 1.157 |
| 20 | 2.9430 ±0.0004 | 2.9426 ±0.0008 | 2.9432 ±0.0006 | 2.9429 ±0.0006 | 1.141 |
| 25 | 2.9496 ±0.0004 | 2.9499 ±0.0005 | 2.9492 ±0.0006 | 2.9496 ±0.0005 | 1.123 |
| 30 | 2.9584 ±0.0003 | 2.9577 ±0.0009 | 2.9580 ±0.0008 | 2.9580 ±0.0008 | 1.102 |
| 35 | 2.9677 ±0.0005 | 2.9663 ±0.0014 | 2.9677 ±0.0010 | 2.9672 ±0.0010 | 1.078 |
| 40 | 2.9775 ±0.0006 | 2.9773 ±0.0005 | 2.9781 ±0.0008 | 2.9776 ±0.0007 | 1.053 |
| 45 | 2.9887 ±0.0006 | 2.9879 ±0.0008 | 2.9884 ±0.0008 | 2.9884 ±0.0008 | 1.027 |
| 50 | 3.0010 ±0.0006 | 3.0005 ±0.0007 | 3.0005 ±0.0011 | 3.0007 ±0.0008 | 0.998 |
| 55 | 3.0143 ±0.0006 | 3.0136 ±0.0006 | 3.0146 ±0.0006 | 3.0142 ±0.0006 | .968 |
| 60 | 3.0279 ±0.0007 | 3.0282 ±0.0017 | 3.0284 ±0.0007 | 3.0282 ±0.0011 | .937 |

[a] Arithmetical mean deviation.

TABLE 9.—*Numerical values of the first dissociation constant of o-phthalic acid obtained by different workers at 18° and 25° C*

| Year | Observer and reference | Method | $K_1 \times 10^3$ | |
|---|---|---|---|---|
| | | | 18°C | 25°C |
| 1889 | W. Ostwald, Z. physik. Chem. **3**, 369 (1889) | Conductivity | 1.21 | ------ |
| 1891 | D. Berthelot, Ann. chim. phys. [6] **23**, 5 (1891) | do | 1.25 | ------ |
| 1892 | J. E. Trevor, Z. physik. Chem. **10**, 321 (1892) | Sucrose inversion | ------ | 1.21 |
| 1908 | E. E. Chandler, J. Am. Chem. Soc. **30**, 694 (1908) | Conductivity | ------ | 1.21 |
| 1908 | E. Salm, Z. physik. Chem. **62**, 83 (1908) | Indicators | ------ | 1.3 |
| [b]1909 | G. F. White and H. C. Jones, Am. Chem. J. **42**, 520 (1909). | Conductivity | ------ | 1.26 |
| 1910 | A. C. D. Rivett and N. V. Sidgwick, J. Chem. Soc. **97**, 1677 (1910). | Velocity of hydration of the anhydride. | ------ | 1.21 |
| 1924 | E. Larsson, Z. anorg. allgem. Chem. **140**, 292 (1924) | Potentiometric titration | 1.20 | ------ |
| 1925 | M. Mizutani, Z. physik. chem. **118**, 318 (1925) | do | [b]1.7 | ------ |
| 1928 | R. Kuhn and A. Wasserman, Helv. chim. Acta **11**, 44 (1928). | emf-quinhydrone electrode | ------ | 1.3 |
| 1929 | A. Ölander, Z. physik. Chem. Abt. [A] **144**, 49 (1929) | Potentiometric titration | ------ | [c]1.0 |
| 1935 | W. R. Maxwell and J. R. Partington, Trans. Faraday Soc. **31**, 922 (1935). | do | ------ | 1.05 |
| 1945 | Present investigation | Galvanic cells without liquid junction. | [d]1.149 | 1.123 |

[a] These authors obtained 0.00134 and 0.00122 for $K_1$ at 0° and 35° C, respectively.
[b] Value for 20° C.
[c] Value for 50° C.
[d] Value calculated by eq 19.

In figure 5, the values of $pK_1$ are shown plotted as a function of the temperature in degrees centigrade. This variation may be expressed by the Harned-Robinson [17] equation

$$pK_1 = A^*/T + B + CT. \tag{18}$$

The constants of this equation were obtained by the method of least squares by using the average values of $pK_1$ given in column 5 of table 8. The values of $pK_1$ are given with a mean deviation of 0.0003 by the equation

$$pK_1 = 561.57/T - 1.2843 + 0.0078833T, \tag{19}$$

where $T = t°\ C + 273.16$.

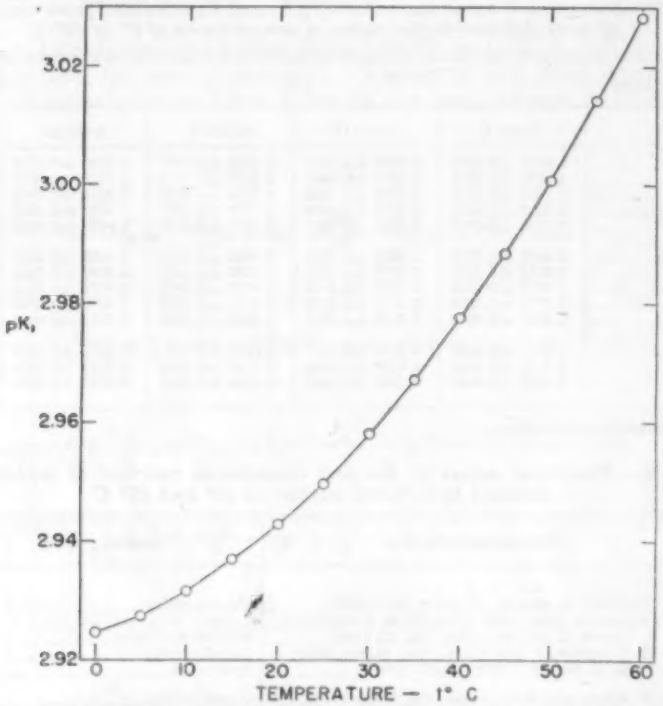


FIGURE 5.—*Plot of the average values of* $pK_1$ *with respect to temperature in degrees centigrade.*

## V. THERMODYNAMIC QUANTITIES FOR THE PROCESS: o-PHTHALIC ACID⇄HYDROGEN ION+ACID PHTHALATE ION

Thermodynamic quantities for the process $H_2Ph \rightleftarrows H^+ + HPh^-$ can be computed from the equations of Harned and Robinson. The change in free energy, $\Delta F°$; in heat content, $\Delta H°$; in entropy, $\Delta S°$; and in heat capacity, $\Delta C_p°$; for the dissociation of 1 mole of $H_2Ph$ for the standard state are given, respectively, in international joules by the equations

$$\Delta F° = -RT \ln K_1 = 2.3026R(A^* + BT + CT^2), \\ = 10\,748.9 - 24.5826T + 0.15089T^2 \quad (20)$$

$$\Delta S° = -(d\Delta F°/dT) = 2.3026R(-B - 2CT), \\ = 24.58 - 0.30178T, \quad (21)$$

$$\Delta H° = \Delta F° + T\Delta S° = 2.3026R(A^* - CT^2), \\ = 10748.9 - 0.15089T^2, \quad (22)$$

$$\Delta C_p° = (d\Delta H°/dT) = 2.3026R(-2CT), \\ = -0.3018T, \quad (23)$$

where $A^*$, $B$, and $C$ are the same constants as in eq 18.

These quantities were calculated in terms of the international joule by using a value of 8.3127 int. j $deg^{-1}$ for $R$ [18] and are given in table 10. They were also calculated in terms of a defined calorie, 1 cal being taken equal to 4.1833 int. j, in accordance with the recommendation of the Internation Union of Chemistry [19,20].

These are also listed in table 10. The values of $\Delta C_p^\circ$ increase slightly with temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [21]. Values of $\Delta F^\circ$ and $\Delta S^\circ$ also increase with respect to temperature.

TABLE 10.—*Thermodynamic data from 0° to 60° C for the dissociation of o-phthalic acid into hydrogen and acid phthalate ions*

| t°C | $\Delta F^\circ$ | | $\Delta H^\circ$ | | $\Delta S^\circ$ | | $\Delta C_p^\circ$ | |
|---|---|---|---|---|---|---|---|---|
| | *Int. j* | *cal* | *Int. j* | *cal* | *Int. j* | *cal* | *Int. j* | *cal* |
| 0 | 15,293 | 3,656 | −510 | −122 | −57.9 | −13.8 | −82.4 | −19.7 |
| 5 | 15,586 | 3,726 | −926 | −221 | −59.4 | −14.2 | −84.0 | −20.1 |
| 10 | 15,896 | 3,798 | −1,349 | −323 | −60.9 | −14.6 | −85.5 | −20.4 |
| 15 | 16,195 | 3,871 | −1,780 | −426 | −61.4 | −14.7 | −87.0 | −20.8 |
| 20 | 16,510 | 3,947 | −2,219 | −530 | −63.9 | −15.3 | −88.5 | −21.2 |
| 25 | 16,833 | 4,024 | −2,665 | −637 | −65.4 | −15.6 | −90.0 | −21.5 |
| 30 | 17,164 | 4,103 | −3,119 | −746 | −66.9 | −16.0 | −91.5 | −21.9 |
| 35 | 17,502 | 4,184 | −3,580 | −856 | −68.4 | −16.4 | −93.0 | −22.2 |
| 40 | 17,848 | 4,267 | −4,049 | −968 | −69.9 | −16.7 | −94.5 | −22.6 |
| 45 | 18,202 | 4,351 | −4,525 | −1,082 | −72.4 | −17.3 | −96.0 | −23.0 |
| 50 | 18,563 | 4,437 | −5,009 | −1,197 | −72.9 | −17.4 | −97.5 | −23.3 |
| 55 | 18,931 | 4,525 | −5,500 | −1,315 | −74.5 | −17.8 | −99.0 | −23.7 |
| 60 | 19,307 | 4,615 | −5,999 | −1,434 | −76.0 | −18.2 | −100.6 | −24.0 |

The values of $\Delta F^\circ$ are obtained directly from those for $K_1$. The uncertainties in $K_1$ introduce deviations in the values of $\Delta F^\circ$ of only 0.1 percent, or about 17 int. j or 4 calories. The values of $\Delta H^\circ$ and $\Delta C_p^\circ$ are subject to large error, estimated to be of the order of 100 calories in $\Delta H^\circ$ and 3 calories in $\Delta C_p^\circ$. The error in $\Delta S^\circ$ is determined by the uncertainties in $\Delta H^\circ$ and $\Delta C_p^\circ$ and is approximately 0.3 calorie.

Unfortunately, no calorimetric measurements have been made of the heat of dissociation of *o*-phthalic acid or of the heat capacities of the ions and molecule involved in the dissociation with which comparisons may be made. However, certain comparisons may be made with similar data obtained for the first dissociation of other acids. Pitzer [22] found from theoretical considerations that $\Delta C_p^\circ$ and $\Delta S^\circ$ are respectively −40 cal/deg and −22 cal for the dissociation of molecules into ions. Experimental measurements [23] for a great number of monobasic acids agree very well with these values. However for the first dissociation of *o*-phthalic acid $\Delta C_p^\circ$ is −21.5 cal/deg which is about one-half the theoretical value given by Pitzer. However inductive and tautomeric effects in phthalic acid (substituted benzoic acid) will tend to increase the electrostatic potential at the carboxyl group [24] producing an orientation of the solvent ($H_2O$) molecules near the surface of the carboxyl groups. Also the steric factors will tend to reduce the value of $\Delta C_p^\circ$, the tendency being most marked for substitution in the orthoposition because of a greater effect on the orientation of the solvent molecules near the carboxyl groups [24].

Everett and Wynne-Jones [24] determined the value of $\Delta C_p^\circ$ for a number of substituted benzoic acids. They found that the meta- and para-substituted acids had values of $\Delta C_p^\circ$ of about −37 cal/deg, whereas, the orthosubstituted acids had values of $\Delta C_p^\circ$ of about −25 cal/deg, on the average. As *o*-phthalic acid may be considered to be carboxylic-substituted benzoic acid, its value of $\Delta C_p^\circ$ of −21.5 cal/deg is in line with the values for other orthosubstituted benzoic acids.

In table 11, a comparison of $\Delta C_p^\circ$ and $\Delta S^\circ$ for a number of ortho-substituted benzoic acids is given. With the exception of salicylic acid, the data of the different acids are almost the same. Everett and Wynne-Jones state that the $OH^-$ group favors the orientation of the water molecule, probably because the hydroxyl group forms a hydrogen bond with the oxygen of a water molecule. Therefore, the $\Delta C_p^\circ$ value will be higher for salicylic acid than for those acids not capable of producing hydrogen bonding. The value of $\Delta S^\circ$ for *o*-phthalic acid is somewhat less than that for the other substituted acids. The reason for this is not quite clear. However, within the experimental error with which $\Delta S^\circ$ is determined in the two sets of measurements, the values may be considered to be within substantial agreement.

TABLE 11.—*Comparison of values of* $\Delta C_p^\circ$, $\Delta S^\circ$, $\Delta F^\circ$, *and* p$K$ *at 25°C for ortho-substituted benzoic acids* [a]

| Substituent | Acid | $\Delta C_p^\circ$ | $\Delta S^\circ$ | $\Delta F^\circ$ | p$K$ |
|---|---|---|---|---|---|
| | | *cal/deg* | *cal/deg* | *cal* | |
| | Benzoic | −36.2 | −18.9 | 5,682 | 4.17 |
| Cl | Chlorobenzoic | −28.3 | −21.5 | 3,926 | 2.88 |
| I | Iodobenzoic | −21.9 | −24.0 | 3,903 | 2.86 |
| $NO_2$ | Nitrobenzoic | −23.7 | −21.3 | 2,980 | 2.18 |
| OH | Salicylic | −47.7 | −10.2 | 4,055 | 2.97 |
| COOH | Phthalic | −21.5 | −15.6 | 4,024 | 2.95 |

[a] All the values are taken from a paper by Everett and Wynne-Jones [24], except those for phthalic acid, which are from the present investigation.

## VI. INTERCARBOXYLIC DISTANCES IN *o*-PHTHALIC ACID

The linear distance $r$ between the ionic centers of the carboxyl groups of a rigid dibasic acid may be computed by the Bjerrum equation [25] [7]

$$\log (K_1/K_2) - \log 4 = \epsilon^2/(2.3026\ DrkT), \qquad [24]$$

where $K_1$ and $K_2$ are the first and second dissociation constants of the dibasic acid, $D$ is the dielectric constant of the solvent, $k$ is the Boltzmann constant ($1.380\times10^{-16}$ erg $deg^{-1}$), $T$ is the absolute temperature, and $\epsilon$ is the electronic charge ($4.8025\times10^{-10}$ abs esu).

Values of $r$ for *o*-phthalic acid were computed by this equation for each temperature by the use of the values of $K_1$ obtained in this investigation and the values of $K_2$ given in another publication [1]. They are given in table 12. Within the experimental error the values are independent of the temperature. The average value of 1.66 A is, as anticipated, somewhat larger than 1.53 A and 1.43 A as found by X-ray measurements for the distances, respectively, between the carbon atoms in the diamond and in benzene, but is of the expected order of magnitude.

[7] More complicated equations may be employed to relate chemical constitution with dissociation constants. See Gustav Kortüm, Elecktrolytlösungen, chap. 15, for a review of these equations. (Akademische Verlagsgesellschaft, Becker & Erler, Kom.-Ges., Leipzig, 1941).

TABLE 12.—*Numerical values of the intercarboxyl distances in o-phthalic acid at temperatures of 0° to 60° C* [a]

| $t$ | $K_1 \times 10^3$ | $K_2 \times 10^6$ | $K_1/K_2$ | $r_1$ *Bjerrum* |
|---|---|---|---|---|
| °C | | | | *Angstroms* |
| 0 | 1.190 | 3.696 | 322 | 1.58 |
| 5 | 1.182 | 3.820 | 309 | 1.60 |
| 10 | 1.171 | 3.894 | 301 | 1.62 |
| 15 | 1.157 | 3.934 | 294 | 1.64 |
| 20 | 1.141 | 3.937 | 290 | 1.66 |
| 25 | 1.123 | 3.906 | 288 | 1.67 |
| 30 | 1.102 | 3.840 | 287 | 1.68 |
| 35 | 1.078 | 3.740 | 288 | 1.69 |
| 40 | 1.053 | 3.611 | 292 | 1.70 |
| 45 | 1.027 | 3.454 | 297 | 1.70 |
| 50 | 0.998 | 3.274 | 305 | 1.70 |
| 55 | .968 | 3.075 | 315 | 1.70 |
| 60 | .937 | 2.875 | 326 | 1.70 |

[a] Distance between $C$ atoms in the diamond=1.53. Distance between $C$ atoms in benzene=1.43.

## VII. pH VALUES OF PHTHALATE-CHLORIDE SOLUTIONS

The pH value of each solution used in the cells was calculated from eq 12 by using

$$-2A\sqrt{\mu}/(1+3.76B\sqrt{\mu})+\beta_{Cl}m_{Cl}+\beta_{H}m_{H}$$

for $\log f_H f_{Cl}$. The pH values for solutions of the various series of experiments are given in tables 13, 14, 15, 16, and 17. The values

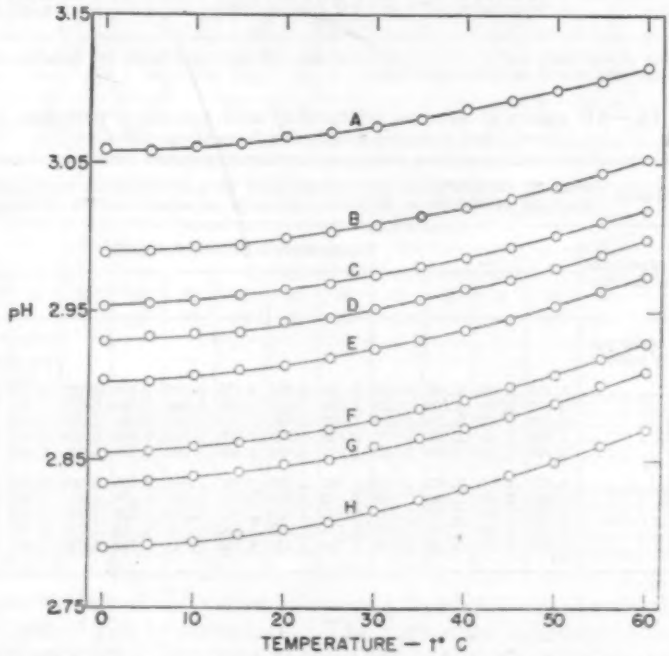


FIGURE 6.—*Plot of a few of the* pH *values of solutions of series I with respect to temperature in degrees centigrade.*

$A$=0.0019071-m KHPh.
$B$=0.0027656-m KHPh.
$C$=0.0034165-m KHPh.
$D$=0.0039521-m KHPh.
$E$=0.0047953-m KHPh.
$F$=0.0068606-m KHPh.
$G$=0.081020-m KHPh.
$H$=0.011799-m KHPh.
Molality of $H_2Ph$=1.5×molality of KHPh and molality of KCl=molality of KHPh.

range from 2.699 to 3.258 and have a low-temperature coefficient. On the average, the pH values differ by 0.07 pH unit between 0° and 60° C.

TABLE 13.—pH *values of aqueous mixtures of acid potassium phthalate, o-phthalic acid and potassium chloride from 0° to 60° C*

SERIES I. {MOLALITY OF o-PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.

| Molality of acid potassium phthalate | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0018357 | 3.066 | 3.066 | 3.068 | 3.072 | 3.075 | 3.078 | 3.084 | 3.089 | 3.094 | 3.101 | 3.109 | 3.116 | 3.124 |
| .0019071 | 3.059 | 3.058 | 3.061 | 3.063 | 3.068 | 3.071 | 3.075 | 3.080 | 3.087 | 3.093 | 3.100 | 3.106 | 3.115 |
| .0027658 | 2.990 | 2.991 | 2.994 | 2.995 | 3.000 | 3.004 | 3.009 | 3.015 | 3.021 | 3.027 | 3.035 | 3.044 | 3.053 |
| .0034165 | 2.953 | 2.955 | 2.957 | 2.961 | 2.965 | 2.969 | 2.975 | 2.981 | 2.987 | 2.994 | 3.002 | 3.011 | 3.019 |
| .0039521 | 2.930 | 2.933 | 2.935 | 2.936 | 2.943 | 2.946 | 2.952 | 2.958 | 2.966 | 2.972 | 2.980 | 2.989 | 2.999 |
| *.0040518 | 2.924 | 2.926 | 2.928 | 2.931 | 2.936 | 2.939 | 2.945 | 2.951 | 2.958 | 2.964 | 2.974 | 2.983 | 2.991 |
| .0046056 | 2.909 | 2.912 | 2.915 | 2.917 | 2.920 | 2.924 | 2.930 | 2.938 | 2.943 | 2.952 | 2.961 | 2.970 | 2.979 |
| .0047953 | 2.904 | 2.903 | 2.907 | 2.911 | 2.914 | 2.919 | 2.925 | 2.931 | 2.938 | 2.945 | 2.954 | 2.964 | 2.974 |
| .0068606 | 2.854 | 2.857 | 2.859 | 2.862 | 2.867 | 2.871 | 2.877 | 2.885 | 2.891 | 2.900 | 2.908 | 2.919 | 2.929 |
| .0079547 | 2.838 | 2.838 | 2.843 | 2.845 | 2.850 | 2.854 | 2.861 | 2.865 | 2.864 | 2.883 | 2.894 | 2.903 | 2.914 |
| .0081020 | 2.835 | 2.837 | 2.840 | 2.843 | 2.848 | 2.851 | 2.860 | 2.866 | 2.873 | 2.881 | 2.890 | 2.902 | 2.911 |
| *.011058 | 2.796 | 2.800 | 2.802 | 2.806 | 2.811 | 2.816 | 2.823 | 2.830 | 2.837 | 2.846 | 2.856 | 2.866 | 2.878 |
| *.011799 | 2.791 | 2.794 | 2.796 | 2.800 | 2.804 | 2.808 | 2.816 | 2.824 | 2.830 | 2.840 | 2.850 | 2.860 | 2.871 |
| *.011913 | 2.790 | 2.793 | 2.795 | 2.799 | 2.804 | 2.807 | 2.815 | 2.826 | 2.831 | 2.839 | 2.849 | 2.850 | 2.871 |
| .012000 | 2.792 | 2.794 | 2.796 | 2.801 | 2.804 | 2.809 | 2.817 | 2.824 | 2.832 | 2.841 | 2.849 | 2.861 | 2.872 |

* Molality of o-phthalic acid=1.5063×molality of acid potassium phthalate and molality of potassium chloride=molality of acid potassium phthalate.

TABLE 14.—pH *values of aqueous mixtures of acid potassium phthalate, o-phthalic acid and potassium chloride from 0° to 60° C*

SERIES II. {MOLALITY OF o-PHTHALIC ACID=2×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.

| Molality of acid potassium phthalate | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0008187 | 3.144 | 3.144 | 3.145 | 3.148 | 3.150 | 3.154 | 3.158 | 3.160 | 3.166 | 3.171 | 3.178 | 3.182 | 3.192 |
| .0014005 | 3.022 | 3.024 | 3.024 | 3.027 | 3.029 | 3.033 | 3.038 | 3.038 | 3.048 | 3.053 | 3.061 | 3.068 | 3.076 |
| .0014548 | 3.013 | 3.014 | 3.016 | 3.019 | 3.022 | 3.026 | 3.030 | 3.034 | 3.036 | 3.045 | 3.052 | 3.060 | 3.069 |
| .0023517 | 2.919 | 2.921 | 2.923 | 2.925 | 2.928 | 2.932 | 2.936 | 2.942 | 2.948 | 2.955 | 2.962 | 2.970 | 2.976 |
| .0024641 | 2.908 | 2.910 | 2.913 | 2.917 | 2.919 | 2.924 | 2.928 | 2.933 | 2.940 | 2.946 | 2.954 | 2.962 | 2.971 |
| .0031025 | 2.871 | 2.870 | 2.873 | 2.876 | 2.880 | 2.883 | 2.887 | 2.894 | 2.900 | 2.908 | 2.914 | 2.923 | 2.931 |
| .0036743 | 2.840 | 2.842 | 2.844 | 2.848 | 2.852 | 2.856 | 2.860 | 2.866 | 2.874 | 2.881 | 2.889 | 2.897 | 2.906 |
| .0050000 | 2.792 | 2.794 | 2.797 | 2.801 | 2.805 | 2.809 | 2.814 | 2.823 | 2.828 | 2.835 | 2.843 | 2.852 | 2.864 |
| .0071782 | 2.745 | 2.745 | 2.747 | 2.750 | 2.754 | 2.759 | 2.764 | 2.773 | 2.780 | 2.788 | 2.796 | 2.806 | 2.816 |
| .0090000 | 2.714 | 2.716 | 2.718 | 2.722 | 2.726 | 2.731 | 2.738 | 2.747 | 2.752 | 2.759 | 2.769 | 2.779 | 2.790 |

TABLE 15.—pH *values of aqueous mixtures of acid potassium phthalate and o-phthalic acid containing various amounts of potassium chloride from 0° to 60° C*

SERIES III. MOLALITY OF o-PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTHALATE=0.018

| Molality of potassium chloride | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.005 | 2.921 | 2.923 | 2.926 | 2.931 | 2.935 | 2.941 | 2.948 | 2.955 | 2.964 | 2.974 | 2.983 | 2.992 | 3.007 |
| .008 | 2.919 | 2.920 | 2.924 | 2.928 | 2.933 | 2.939 | 2.946 | 2.953 | 2.961 | 2.971 | 2.982 | 2.992 | 3.005 |
| .010 | 2.916 | 2.918 | 2.920 | 2.926 | 2.928 | 2.937 | 2.943 | 2.950 | 2.959 | 2.968 | 2.979 | 2.989 | 3.004 |
| .014 | 2.914 | 2.916 | 2.920 | 2.925 | 2.929 | 2.935 | 2.942 | 2.949 | 2.957 | 2.966 | 2.977 | 2.989 | 3.001 |
| .018 | 2.910 | 2.912 | 2.918 | 2.919 | 2.924 | 2.932 | 2.936 | 2.944 | 2.953 | 2.962 | 2.973 | 2.984 | 2.998 |

TABLE 16.—pH *values of aqueous mixtures of acid potassium phthalate and o-phthalic acid containing various amounts of potassium chloride from 0° to 60° C*

SERIES IV. {MOLALITY OF o-PHTHALIC ACID=0.018 / MOLALITY OF ACID POTASSIUM PHTHALATE=0.000

| Molality of potassium chloride | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.003000 | 2.718 | 2.721 | 2.723 | 2.726 | 2.731 | 2.736 | 2.741 | 2.749 | 2.756 | 2.765 | 2.773 | 2.785 | 2.796 |
| .005000 | 2.717 | 2.719 | 2.721 | 2.724 | 2.730 | 2.734 | 2.740 | 2.748 | 2.755 | 2.763 | 2.773 | 2.783 | 2.793 |
| .006985 | 2.716 | 2.717 | 2.720 | 2.723 | 2.728 | 2.733 | 2.739 | 2.746 | 2.754 | 2.761 | 2.771 | 2.782 | 2.792 |
| .009000 | 2.714 | 2.715 | 2.718 | 2.721 | 2.725 | 2.731 | 2.736 | 2.744 | 2.753 | 2.759 | 2.768 | 2.779 | 2.790 |
| .04931 | 2.699 | 2.700 | 2.703 | 2.707 | 2.711 | 2.718 | 2.721 | 2.726 | 2.734 | 2.747 | 2.751 | 2.760 | 2.770 |

TABLE 17.—pH *values of aqueous mixtures of acid potassium phthalate, o-phthalic acid and potassium chloride from 0° to 60° C*

SERIES V. {MOLALITY OF o-PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE / MOLALITY OF POTASSIUM CHLORIDE=1.5×MOLALITY

| Molality of acid potassium phthalate | Temperature in degrees centigrade | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| *Moles of solute per 1,000 g of water* | | | | | | | | | | | | | |
| 0.0009423 | 3.210 | 3.211 | 3.213 | 3.214 | 3.217 | 3.220 | 3.225 | 3.229 | 3.234 | 3.289 | 3.245 | 3.252 | 3.258 |
| .0016280 | 3.090 | 3.090 | 3.091 | 3.094 | 3.098 | 3.101 | 3.105 | 3.112 | 3.117 | 3.121 | 3.130 | 3.137 | 3.145 |
| .0026071 | 3.001 | 3.002 | 3.004 | 3.008 | 3.011 | 3.104 | 3.020 | 3.025 | 3.031 | 3.039 | 3.043 | 3.055 | 3.063 |
| .0030788 | 2.972 | 2.973 | 2.976 | 2.979 | 2.982 | 2.986 | 2.991 | 2.998 | 3.003 | 3.011 | 3.017 | 3.027 | 3.037 |
| .0036444 | 2.942 | 2.943 | 2.946 | 2.950 | 2.954 | 2.957 | 2.963 | 2.971 | 2.977 | 2.983 | 2.992 | 3.001 | 3.010 |
| .0038552 | 2.934 | 2.935 | 2.938 | 2.942 | 2.945 | 2.948 | 2.956 | 2.961 | 2.967 | 2.975 | 2.982 | 2.992 | 3.000 |
| .0041264 | 2.923 | 2.925 | 2.927 | 2.930 | 2.934 | 2.938 | 2.944 | 2.950 | 2.956 | 2.964 | 2.973 | 2.981 | 2.991 |
| .0044082 | 2.913 | 2.913 | 2.917 | 2.921 | 2.924 | 2.929 | 2.934 | 2.941 | 2.948 | 2.956 | 2.963 | 2.972 | 2.982 |
| .0054960 | 2.881 | 2.885 | 2.887 | 2.891 | 2.894 | 2.898 | 2.905 | 2.911 | 2.919 | 2.925 | 2.935 | 2.945 | 2.954 |
| .0056467 | 2.875 | 2.879 | 2.881 | 2.884 | 2.888 | 2.894 | 2.898 | 2.904 | 2.912 | 2.919 | 2.928 | 2.938 | 2.948 |

In figure 6 a few of the values of series I (table 13) are shown plotted as a function of the temperature. The curves for different molalities are almost parallel. The data of the other tables give similar plots.

The values in tables 14 and 15 give the effect of potassium chloride on the pH of solutions containing mixtures of *o*-phthalic acid and acid potassium phthalate. The magnitude of the effect is very small. The pH values for any solution of *o*-phthalic acid potassium phthalate

in the ratio from 2 to 1, with or without potassium chloride, may be interpolated from large-scale plots of the data of tables 13 to 17 with respect to the concentration of acid potassium phthalate.

Each solution may be used as a pH standard. It is proposed that they be prepared either from the NBS Standard Sample of acid potassium phthalate and standardized hydrochloric acid, or from acid potassium phthalate, recrystallized potassium chloride, recrystallized *o*-phthalic acid prepared from resublimed phthalic anhydride, and distilled water of pH 6.7 to 7.3 having a specific conductance not over $1.0\times10^{-6}$ mho. The solutions may be used to calibrate a variety of pH equipment. Solutions of higher concentrations than those reported in this investigation should not be employed in the preparation of pH standards. If so, crystals of phthalic acid will separate out if the temperature falls much below 25° C.

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